SAND2015-5929PE

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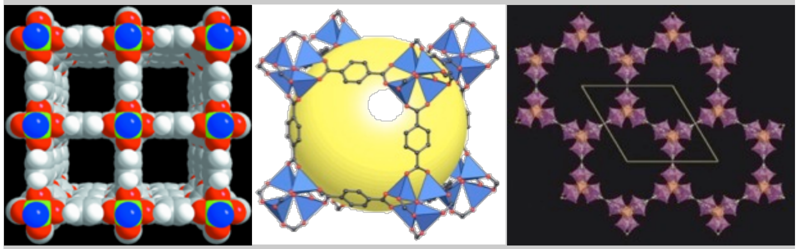

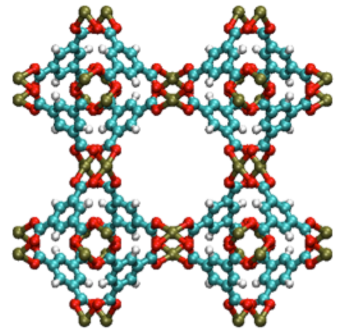

Interactions of Light and Charge with Nanoporous Metal-Organic Frameworks

IEEE SFBA Nanotechnology Council Chapter

July 22, 2015

Mark Allendorf, Senior Scientist

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Transportation Energy Center

Sandia National Laboratories, Livermore, CA

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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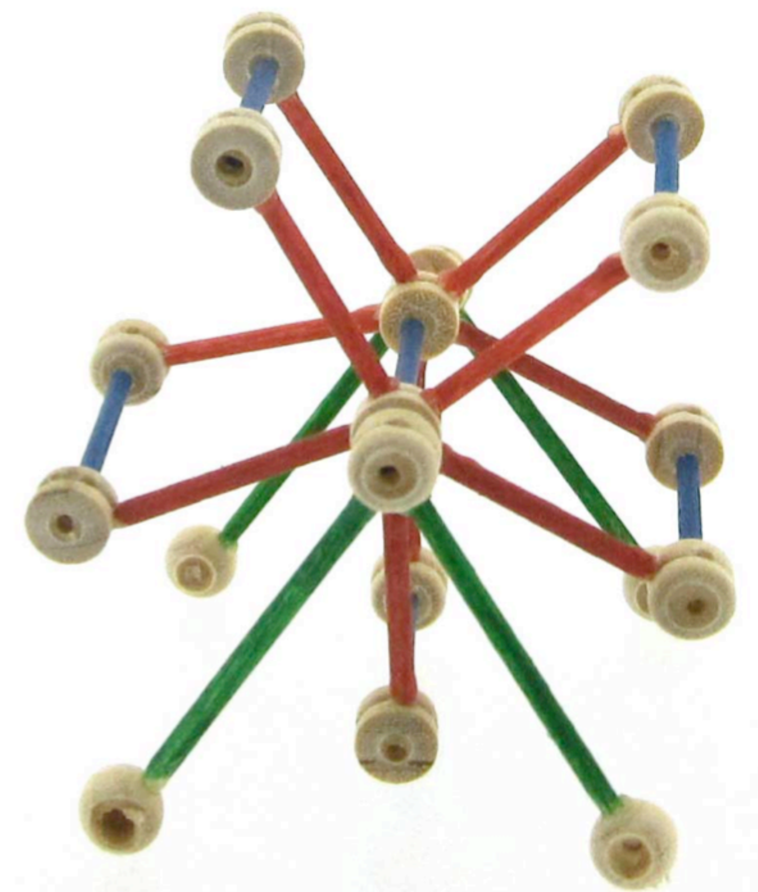
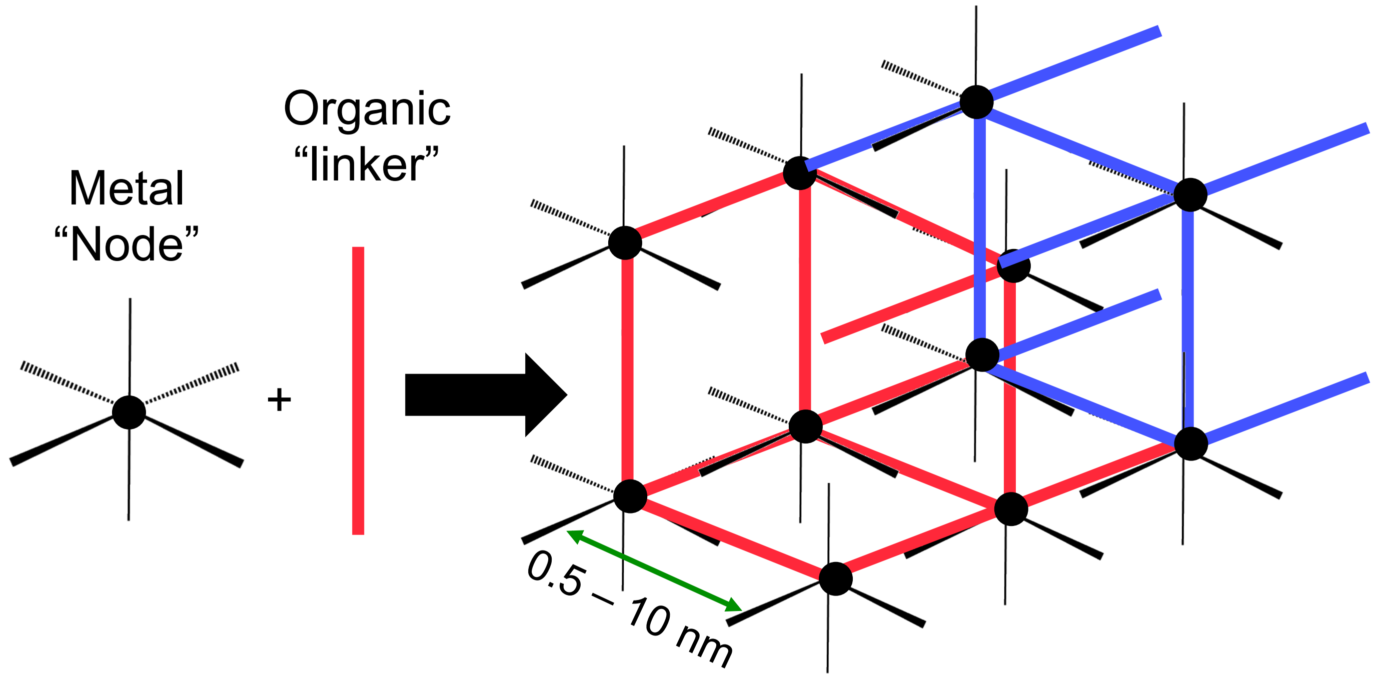
Remember these?

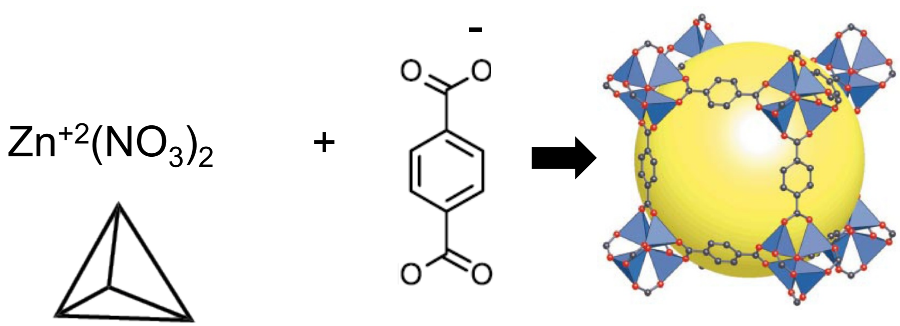


Knowing structure is POWER because it correlates with function

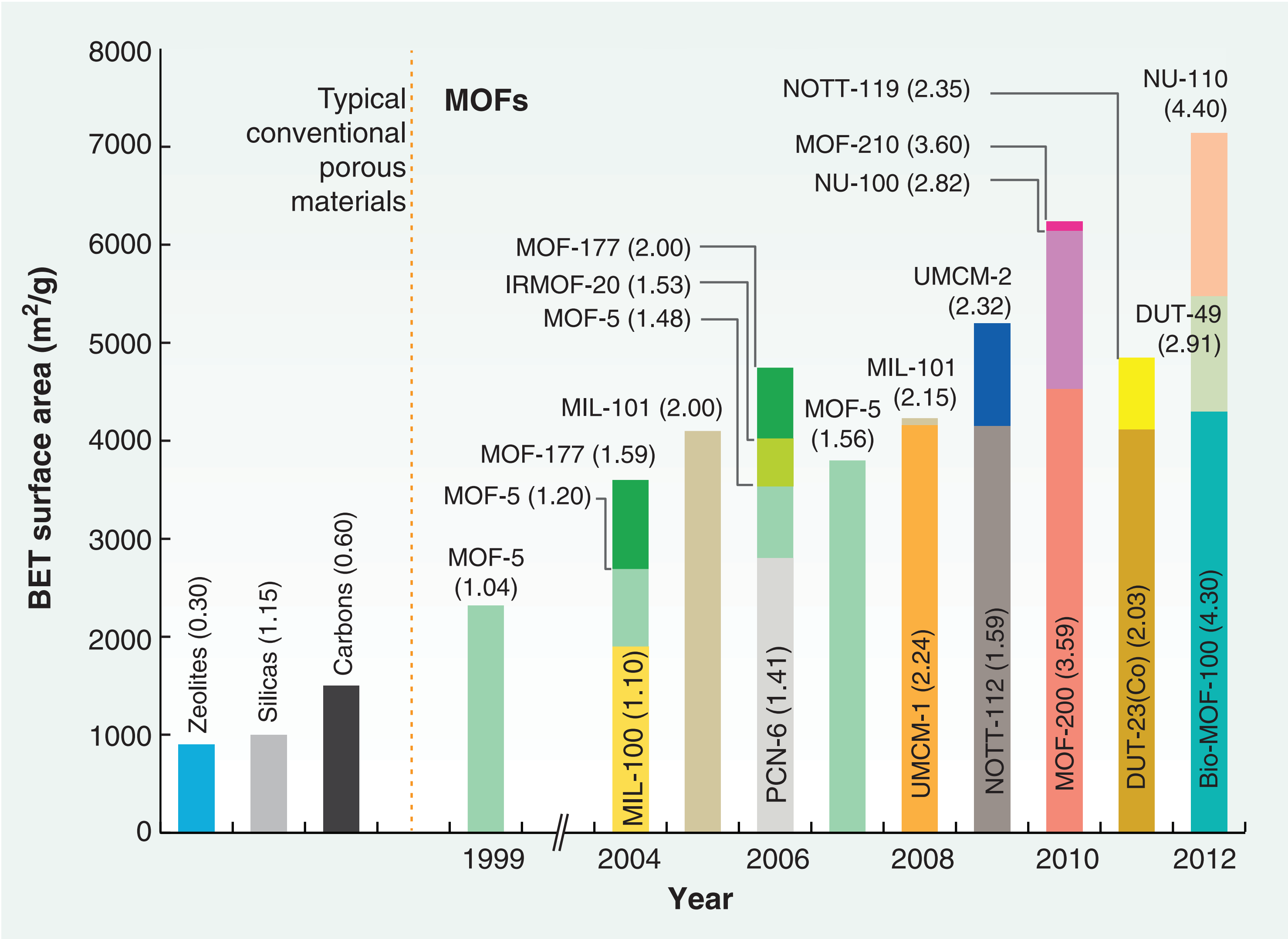
What is a Metal-Organic Framework?

Crystalline (therefore ordered), self-assembled, nanoporous structure



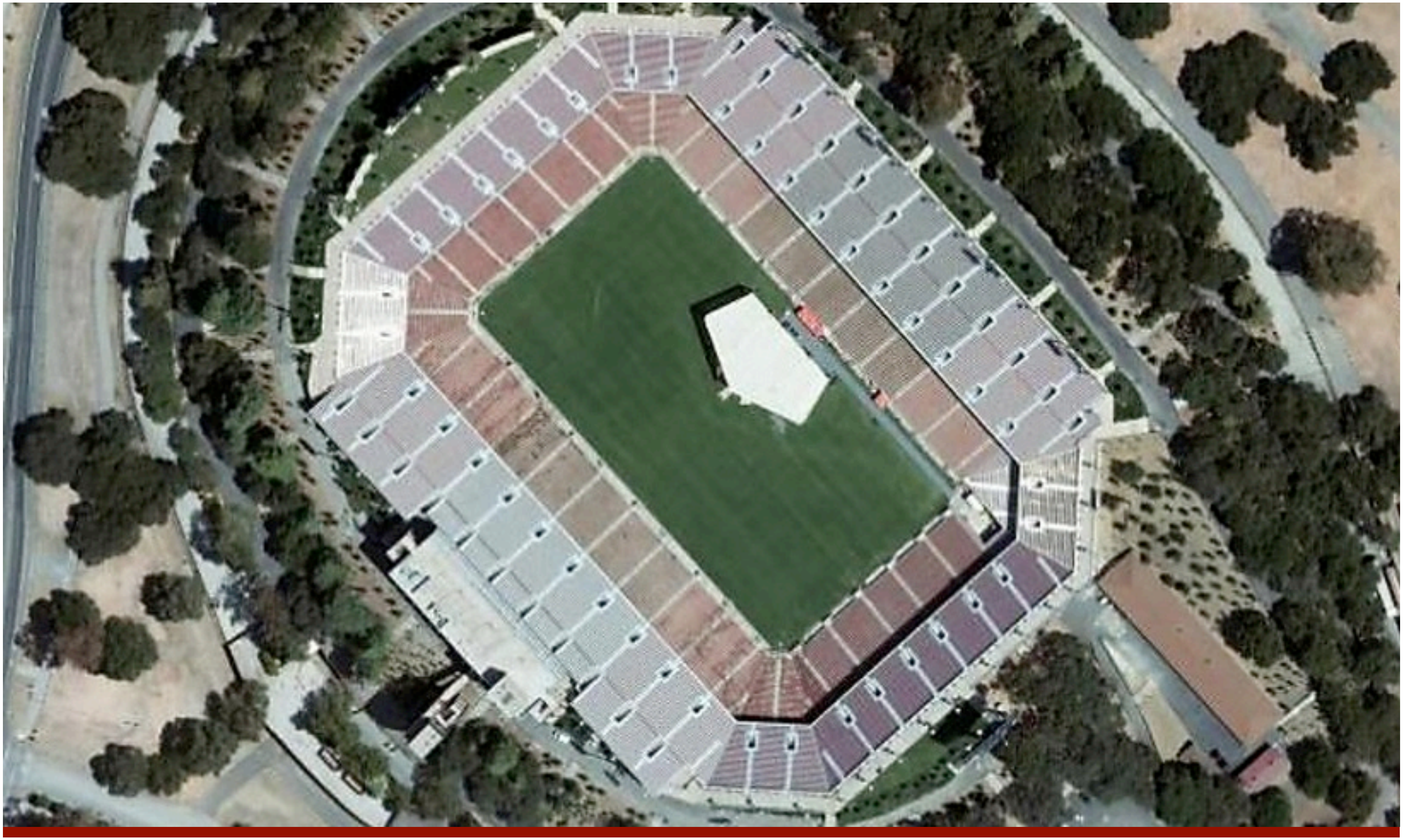


Record surface areas

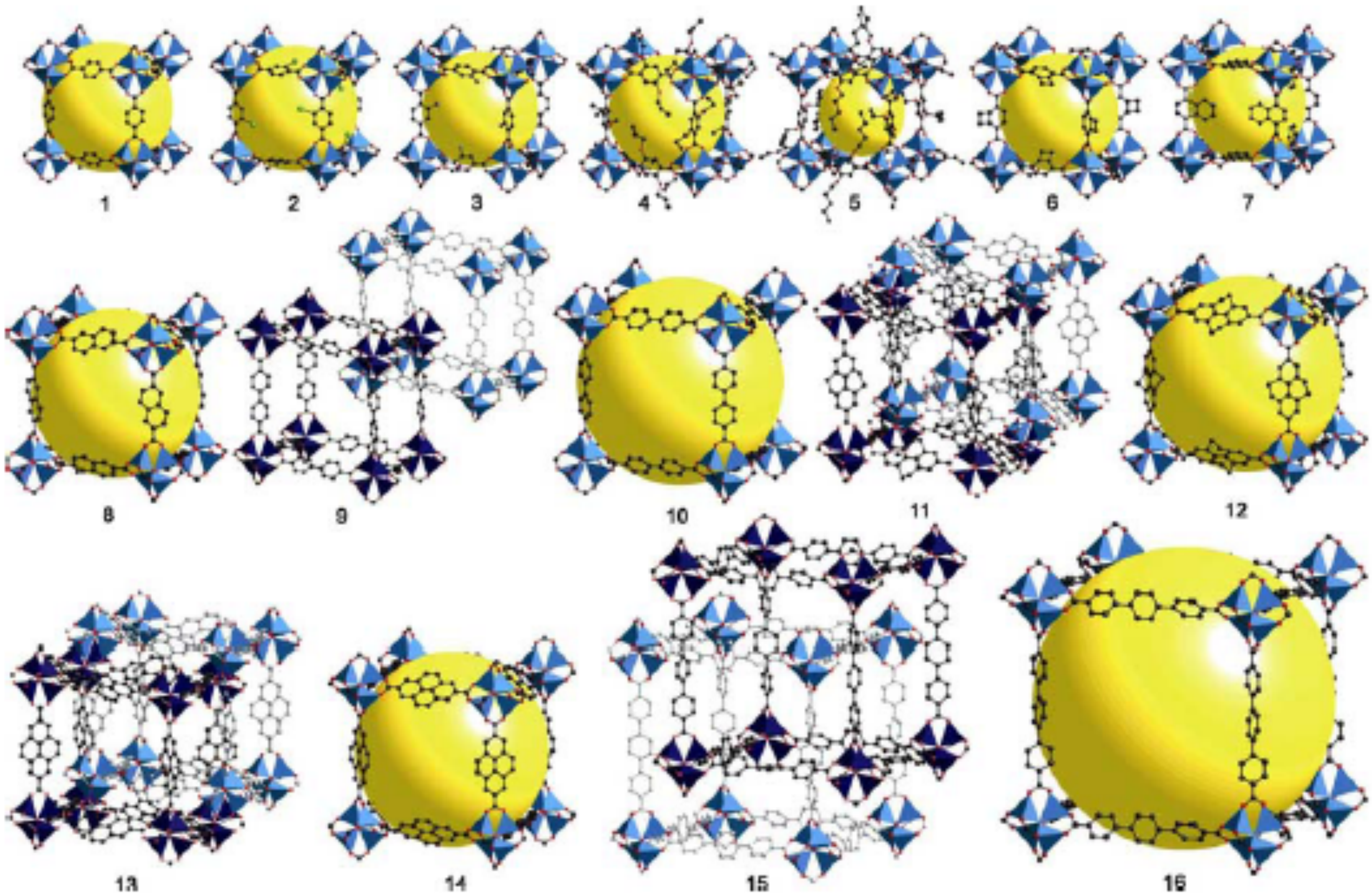


Furukawa et al. *Science* **341**, 974 (2013)

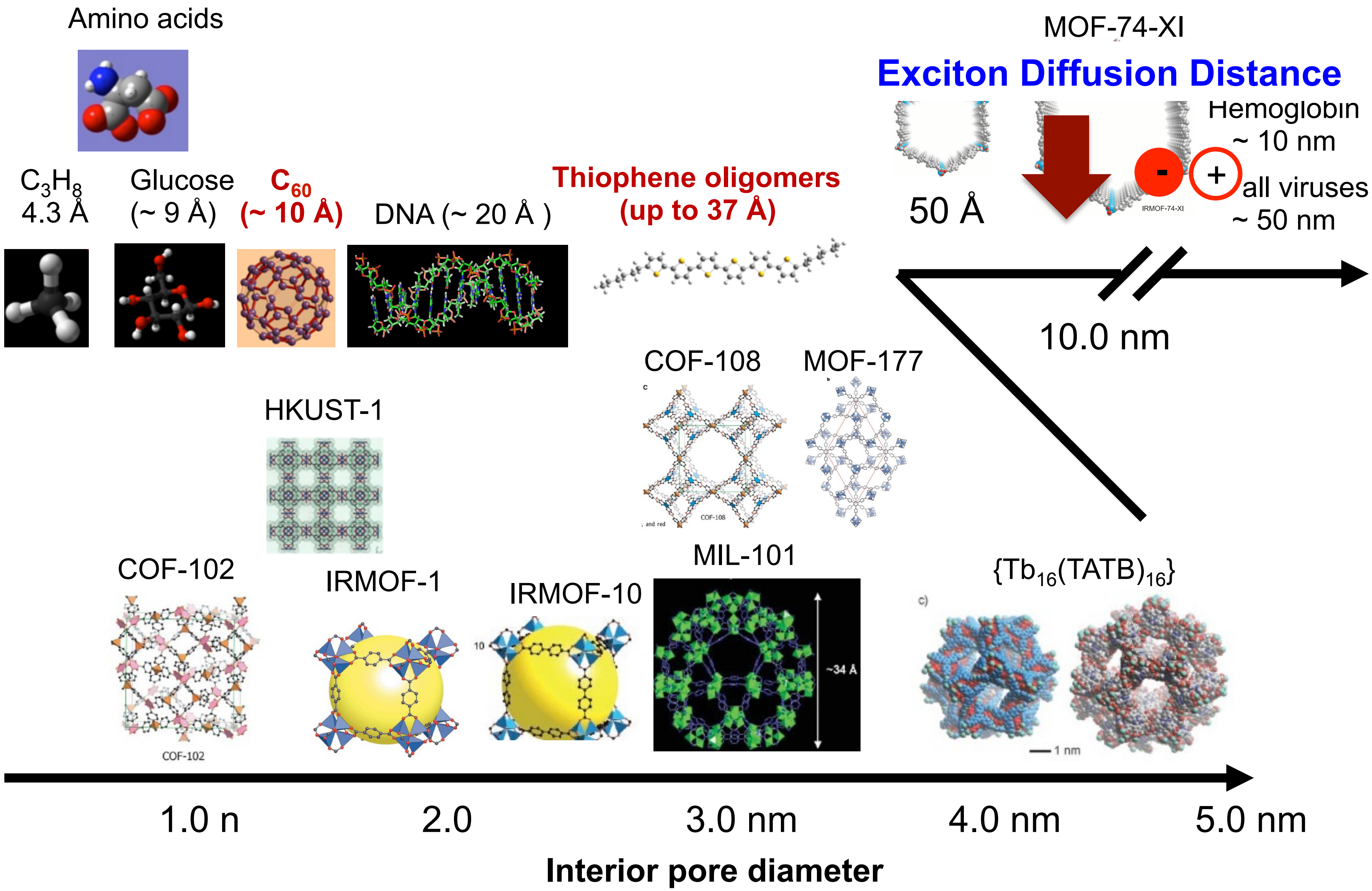
1 football field = 5350 m^2



MOFs are self-assembled, nanoporous materials with tunable pore size and properties

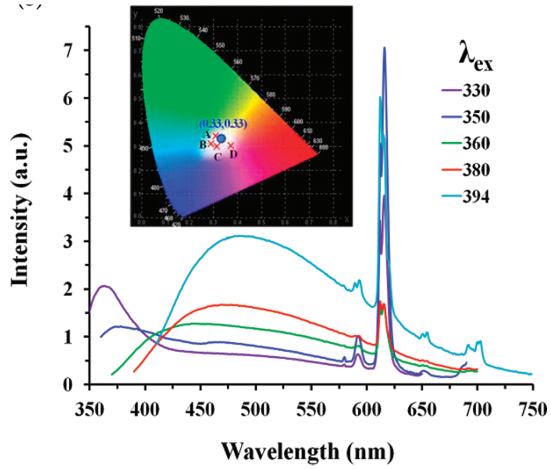


Guest molecule + MOF → ordered, tunable platform for controlling interactions at the nanoscale

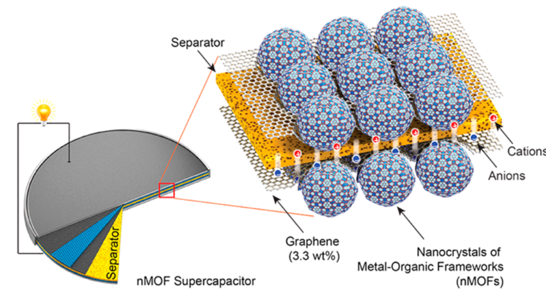


Device applications: the new frontier for MOFs

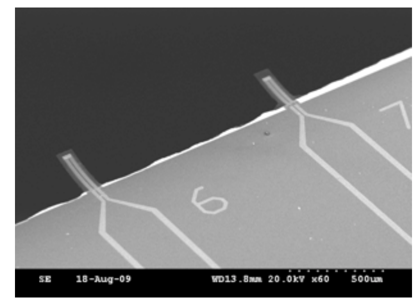
- **Optical**
  - Luminescent
  - Non-linear optical
- **Electronic and magnetic**
  - Dielectric
  - Electrically conducting
  - Ion conducting
  - Ferroelectric
  - Ferromagnetic
  - Antiferromagnetic
  - Spin crossover
  - Ion conducting
- **Mechanical flexibility**



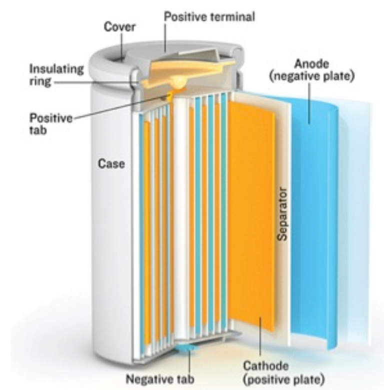
Solid-state lighting
D.F. Sava et al. *JACS* 2012, 134, 3983



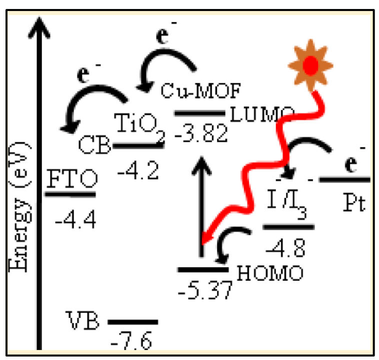
Supercapacitors
K. M. Choi et al. *ACSNano* 2014



Sensors
Allendorf et al.
JACS **2008**, *130*, 14404



Batteries and Fuel Cells
G. Shimizu et al. Chem. Soc. Rev. 2014,**43**, 5913



Photovoltaics
D. Y. Lee et al.
J. Phys. Chem. C **118**, 16328

Our work

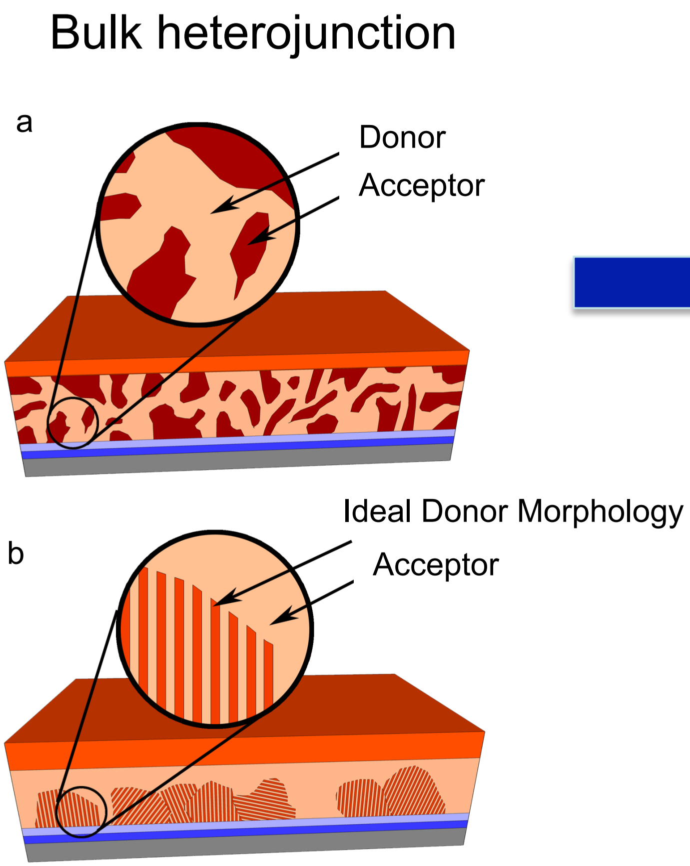
- Thin films
- Energy transfer/photovoltaics
- Radiation detection
- Chemical sensing
- Electrically conducting MOFs

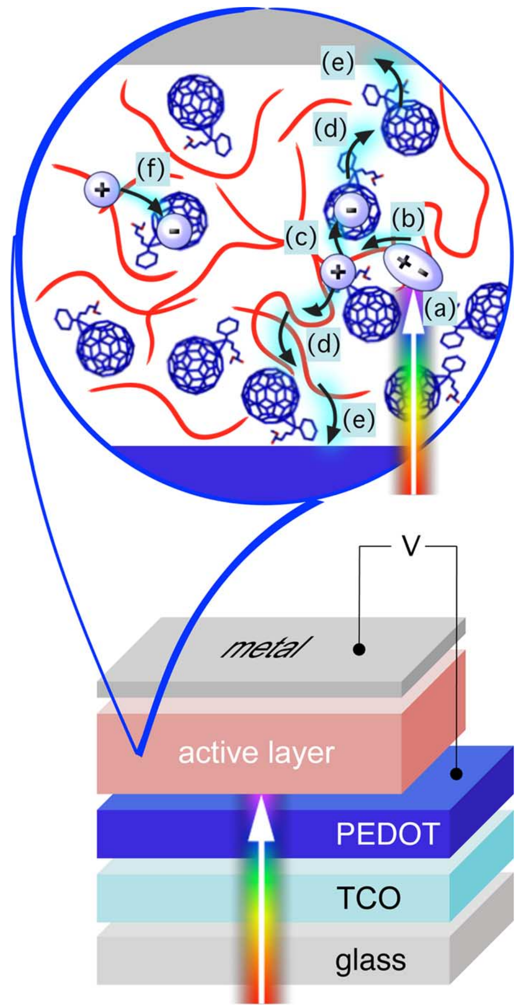
Today's presentation

- Nanoreactors/catalysis
- Hydrogen storage
- Nanoparticle and nanowire templates

Other areas of research

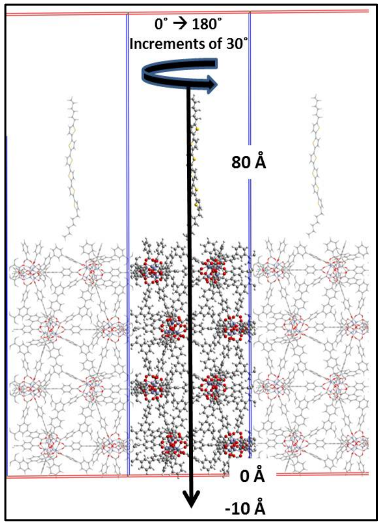
Disorder is the enemy of efficiency

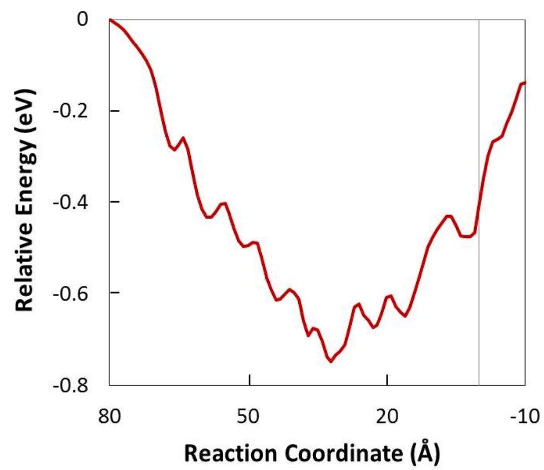


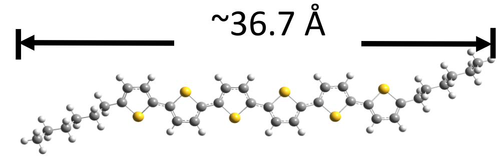


C. Deibel et al. IEEE Journal Of Selected Topics In Quantum Electronics, Vol. 16, No. 6, November/December 2010

Infiltrating MOF-177 pores with thiophenes and PCBM proceeds without an energy barrier

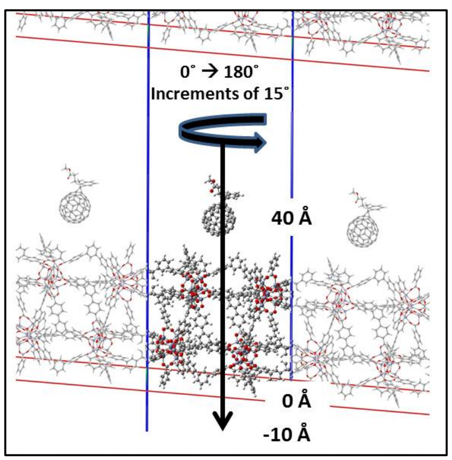


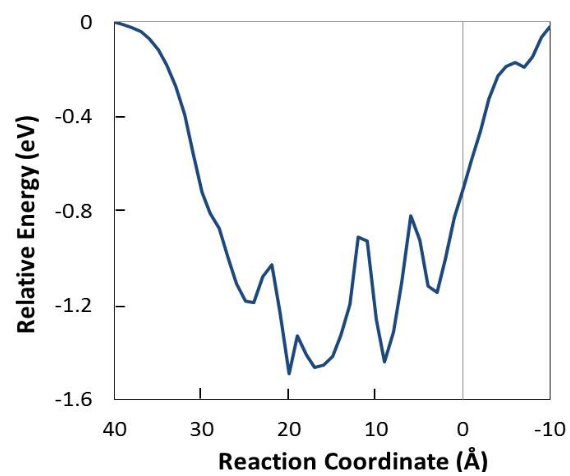


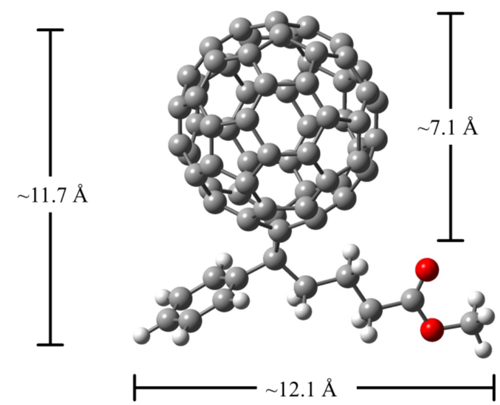


Sexithiophene
Electron Donor

17 kcal/mol B.E.





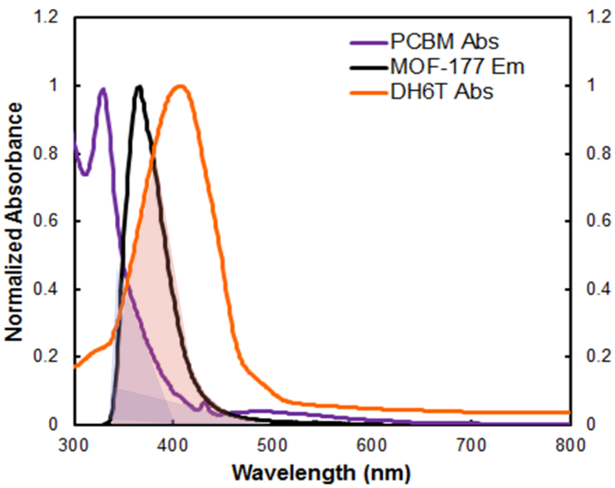


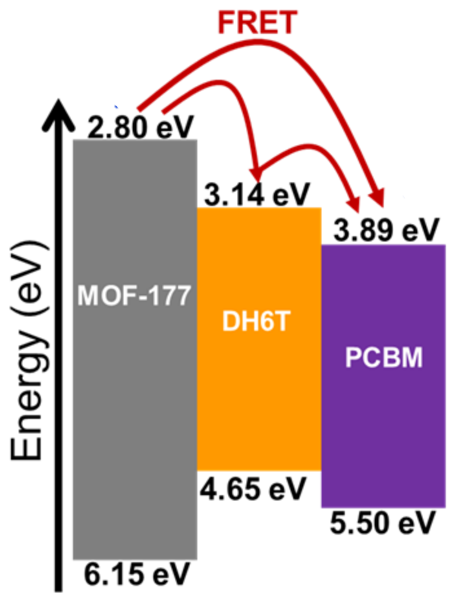
35 kcal/mol B. E.
PCBM
Electron Acceptor

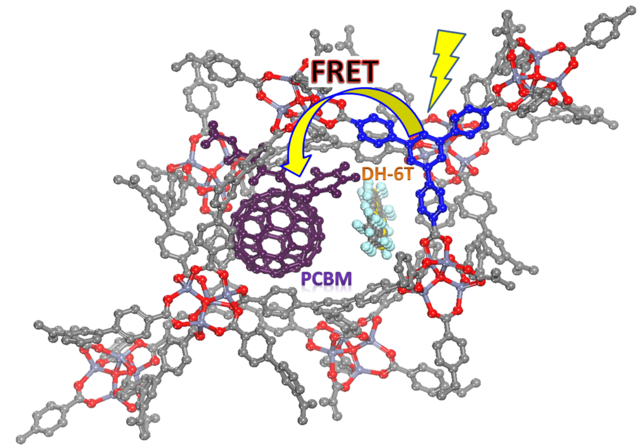
K. Leong et al. *J. Mater. Chem. A,* **2** (2014), 3389

MOF-guest spectral overlap → Fluorescence Resonant Energy Transfer (FRET)

Efficient energy transfer via "FRET cascade" is feasible







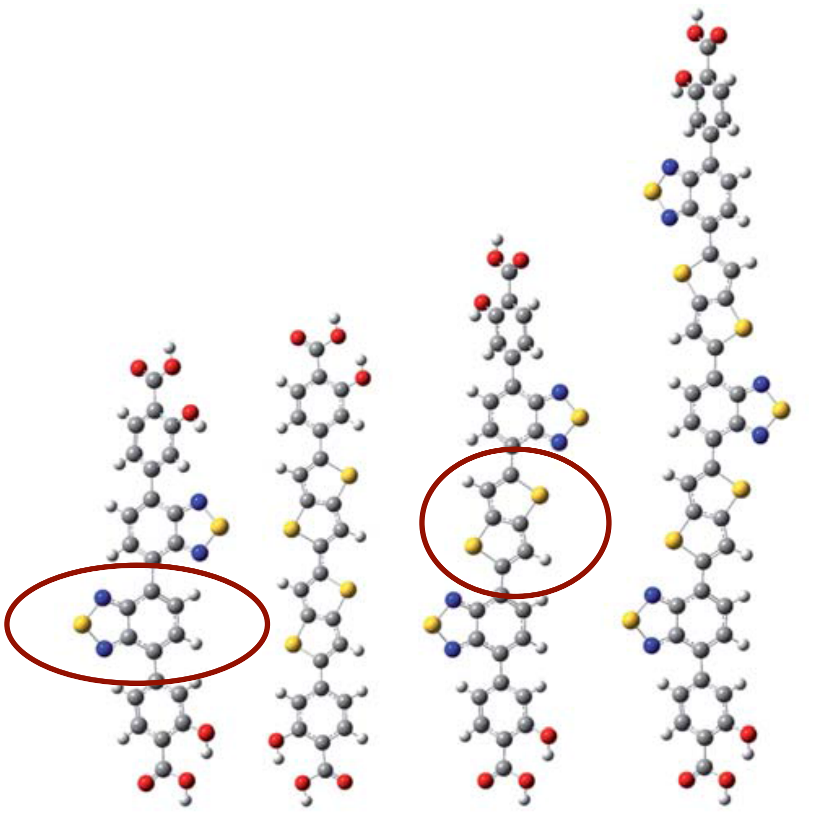
The MOF has three functions:

- Confines/stabilizes donor and acceptor
- Prevents phase segregation
- Serve as a photon antenna

K. Leong et al. *J. Mater. Chem. A,* **2** (2014), 3389

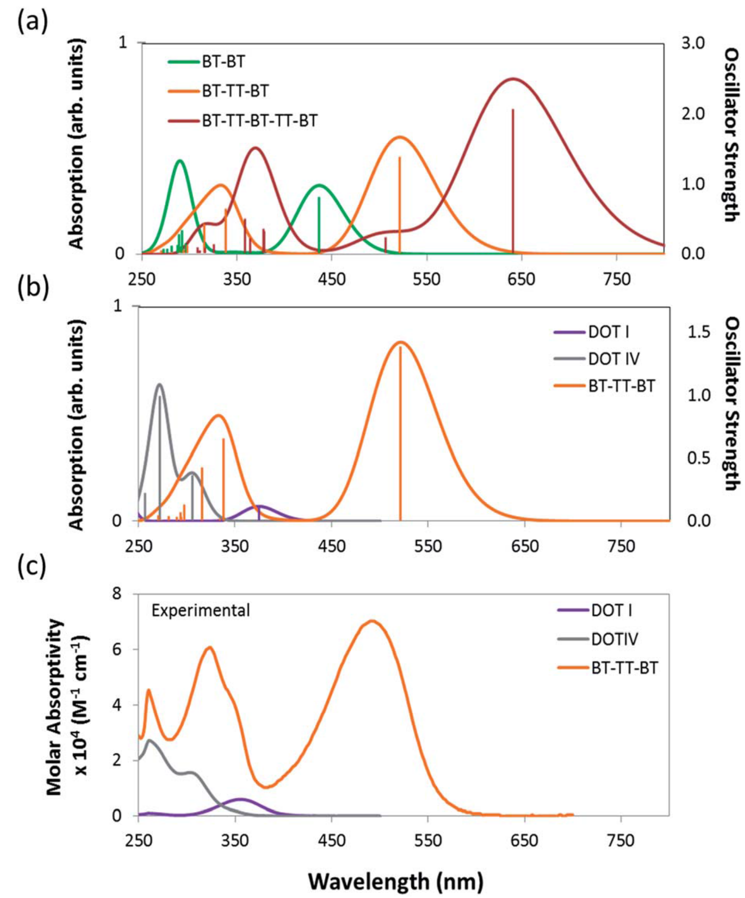
New Donor-Acceptor IRMOF-74 linkers for improved solar coverage

Electron deficient: benzo[c][1,2,5]thiadiazole (BT)
Electron rich: thieno[3,2-b]thiophene (TT)



Foster, Allendorf et al. *Chem. Sci.*, 2014, **5**, 2081

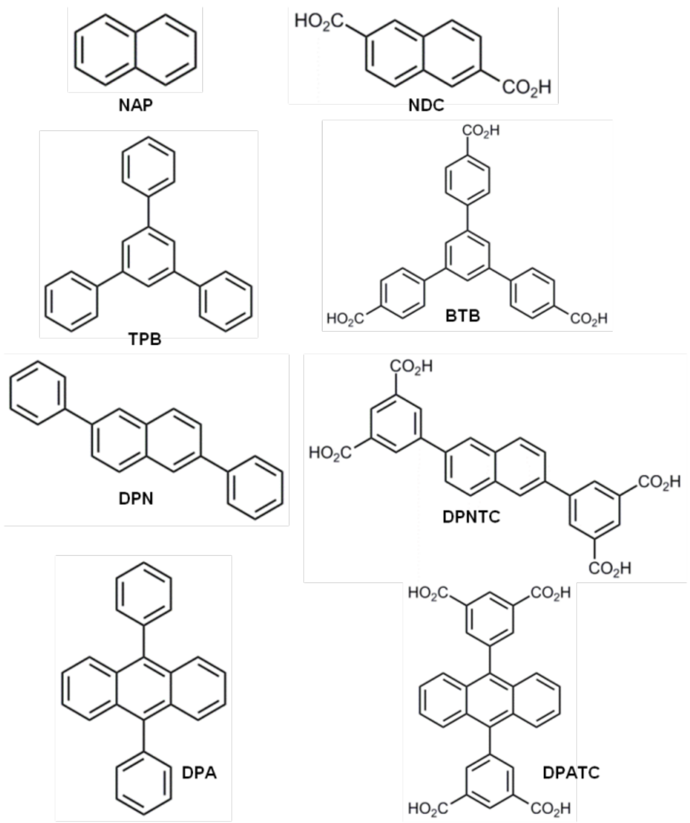
(a,b) Long-range corrected DFT*

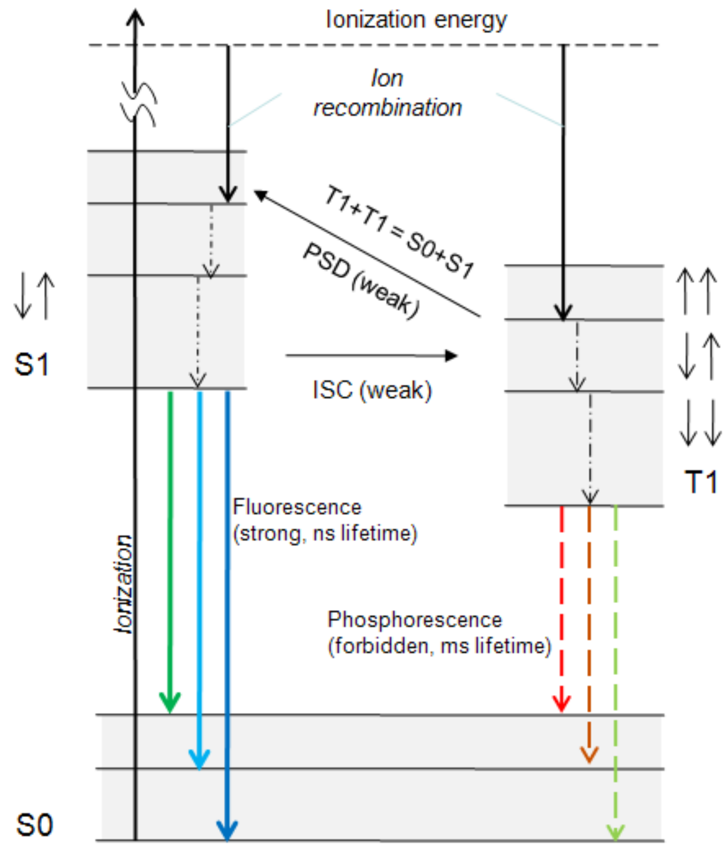


*Non-empirically tuned functional/ time-dependent DFT

Basics of radiation detection using organic scintillators

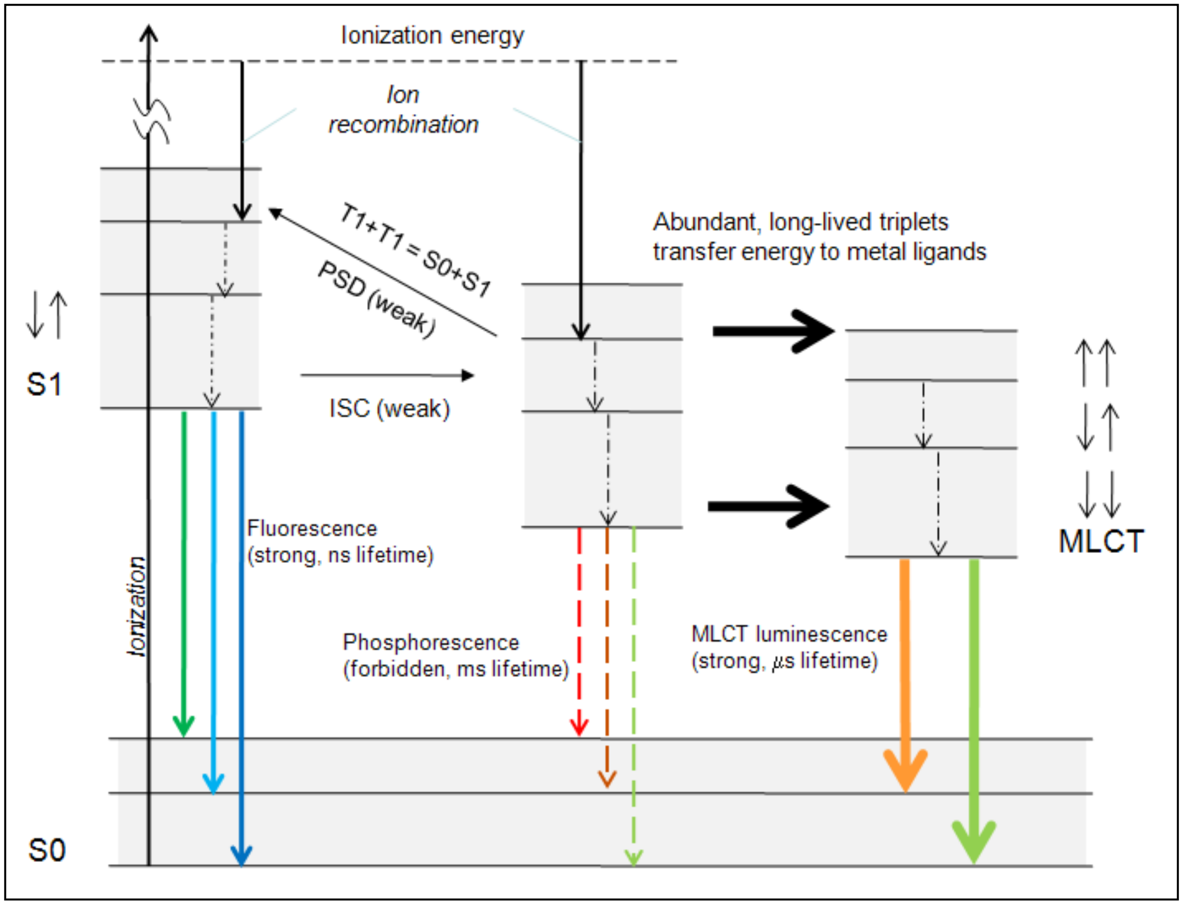
Typical luminescent MOF linkers





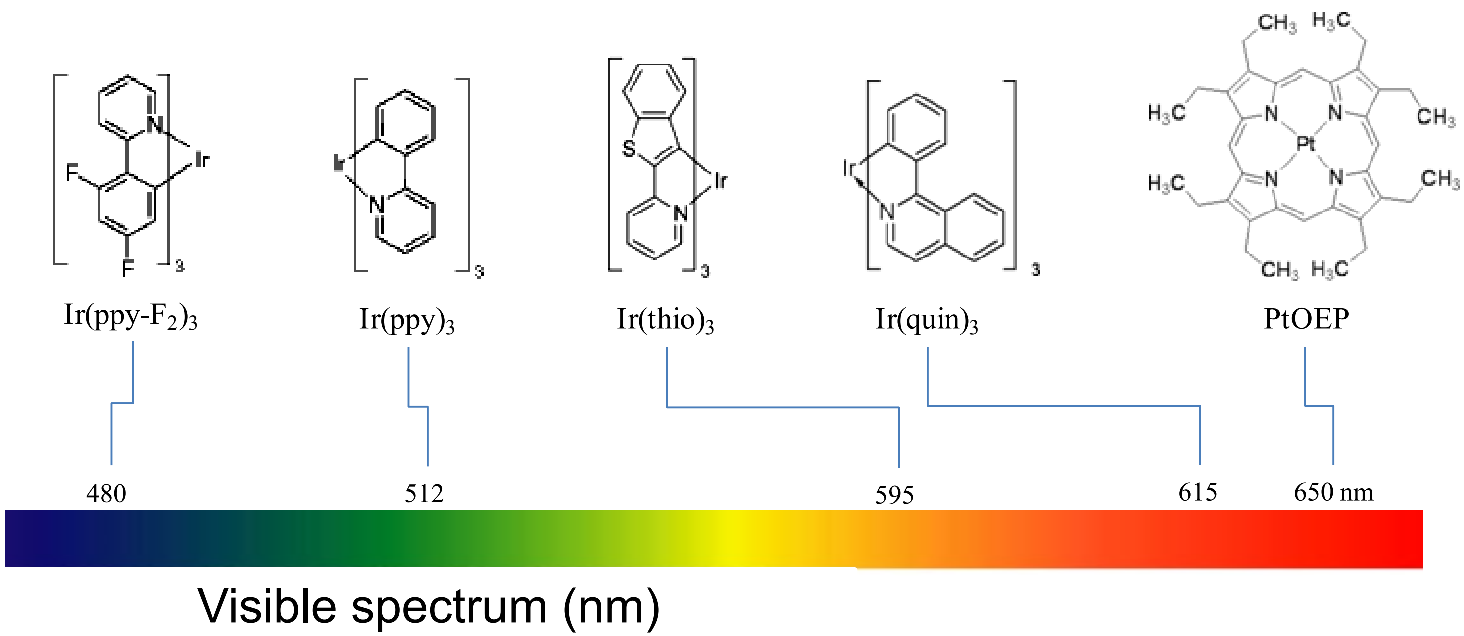
Guest molecules in MOFs create new approach to radiation detection

Ionization creates singlet and triplet excitons, but typically most triplets decay by non-radiative processes



~300% increase in light yield theoretically possible

Triplet harvesting heavy-metal complexes are well known in OLED technology



Extrinsic (Triplet) luminescence: Ir organometallic guest molecules

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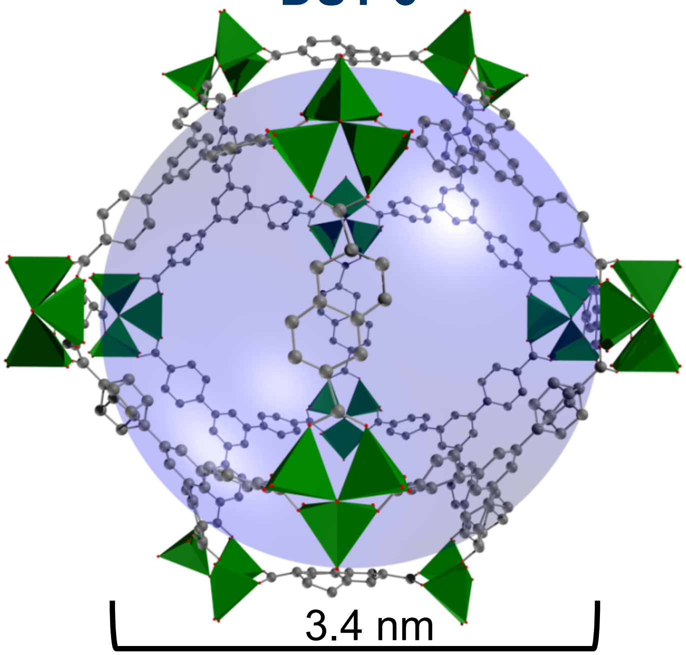
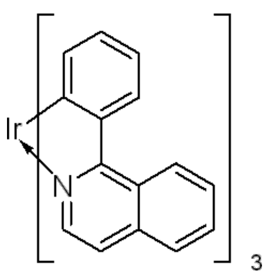
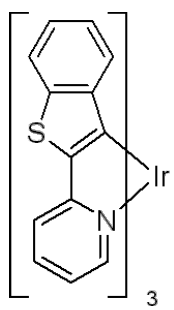
DUT-6

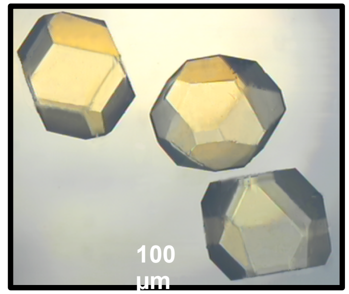


+

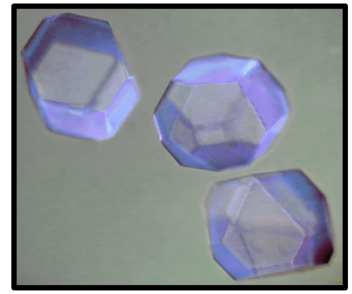


OR





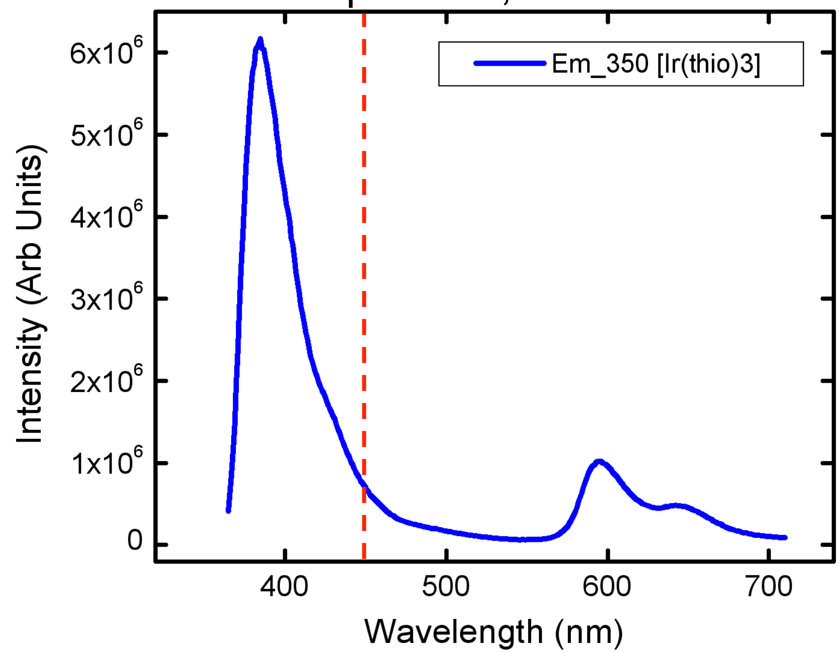
Bright-Field (Vis)



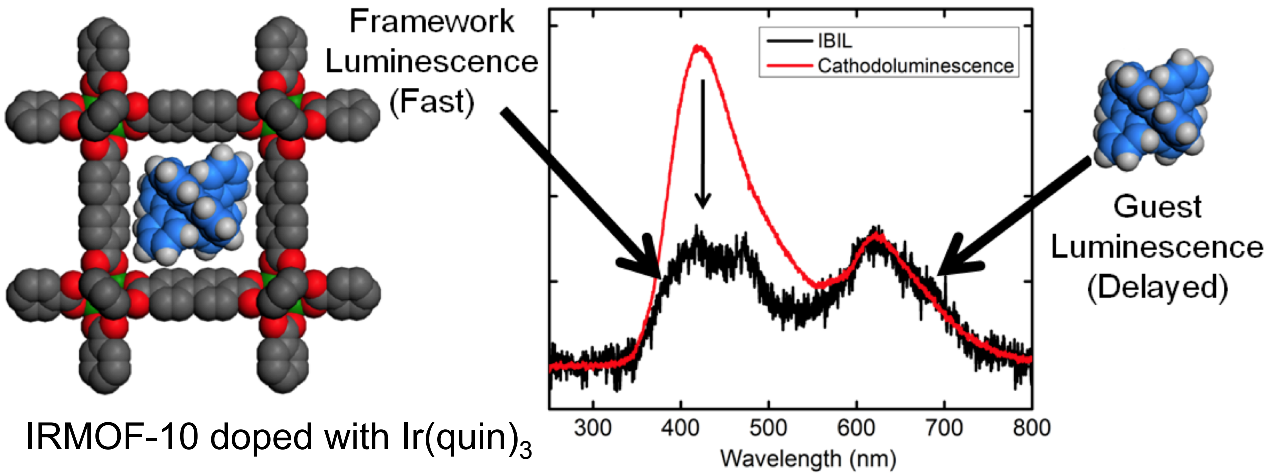
450 nm short-pass

450 nm long-pass

Emission spectrum, 350-nm excitation

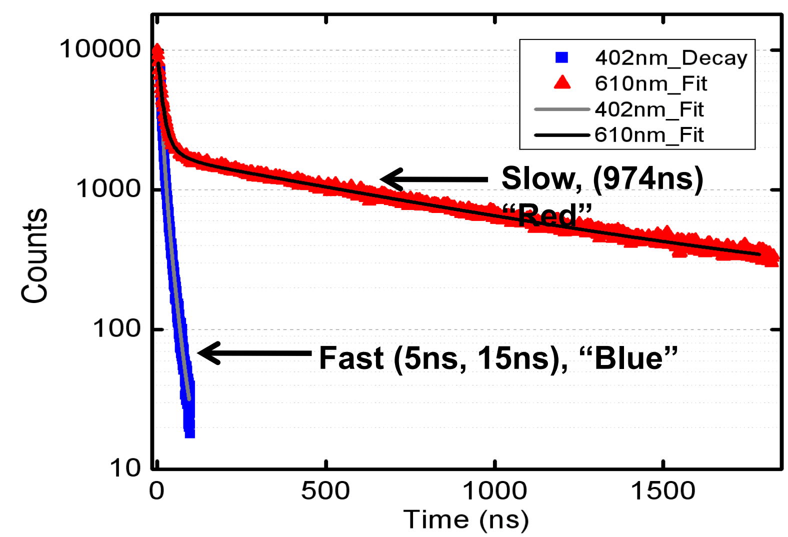


Radiation detection by spectral shape discrimination: IRMOF-10 doped with $Ir(quin)_3$



$[I_{614}/I_{410}]$: PL = **0.11**
$[I_{614}/I_{410}]$: CL = **0.39**
$[I_{614}/I_{410}]$: IBIL = **1.08**

- Sterically matched host-guest combination
- Exponential PL decay times
- Dichroic wavelength selection (SSD) vs. decay time (pulse-shape discrimination)



Layer-by-layer MOF film growth: liquid-phase epitaxy

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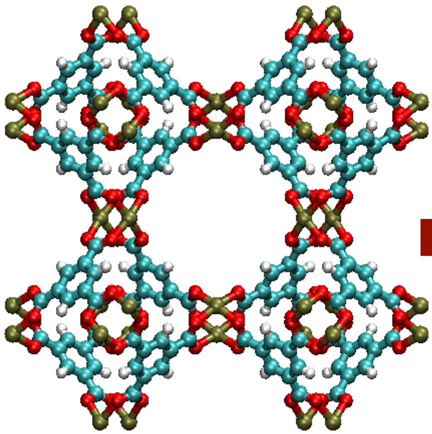
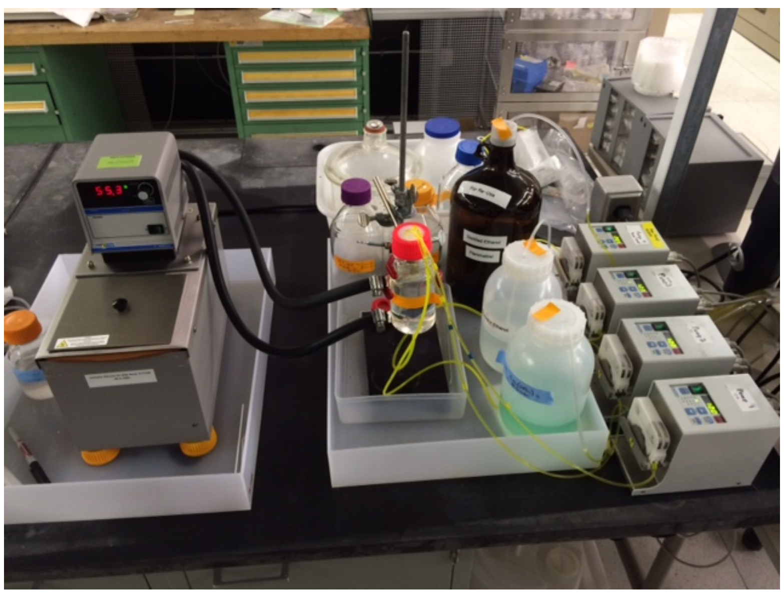
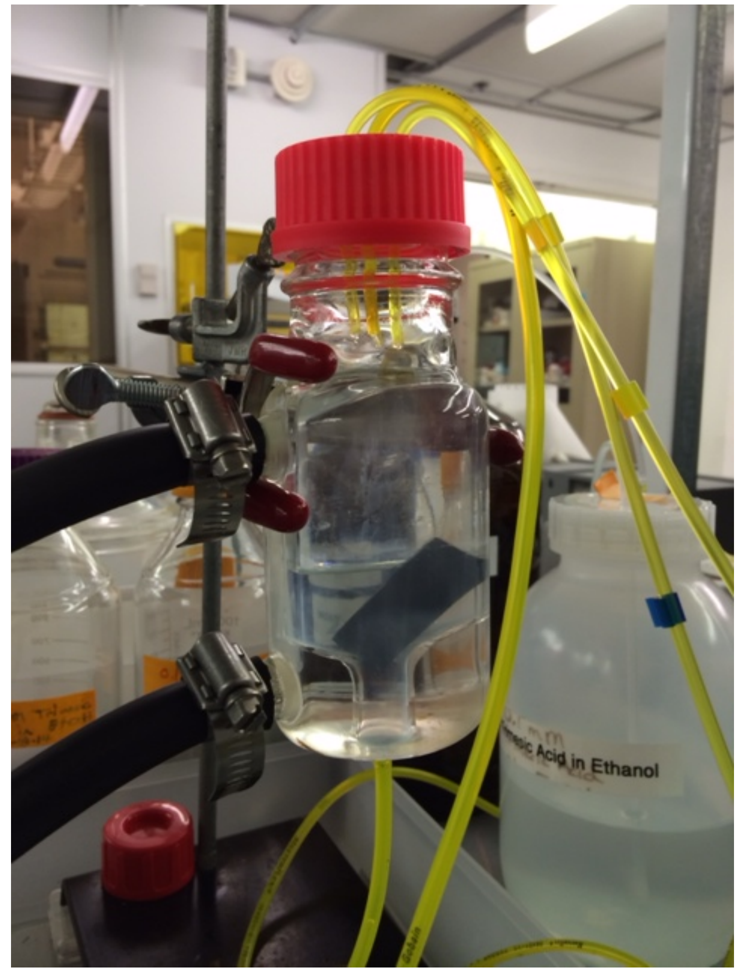
HKUST-1



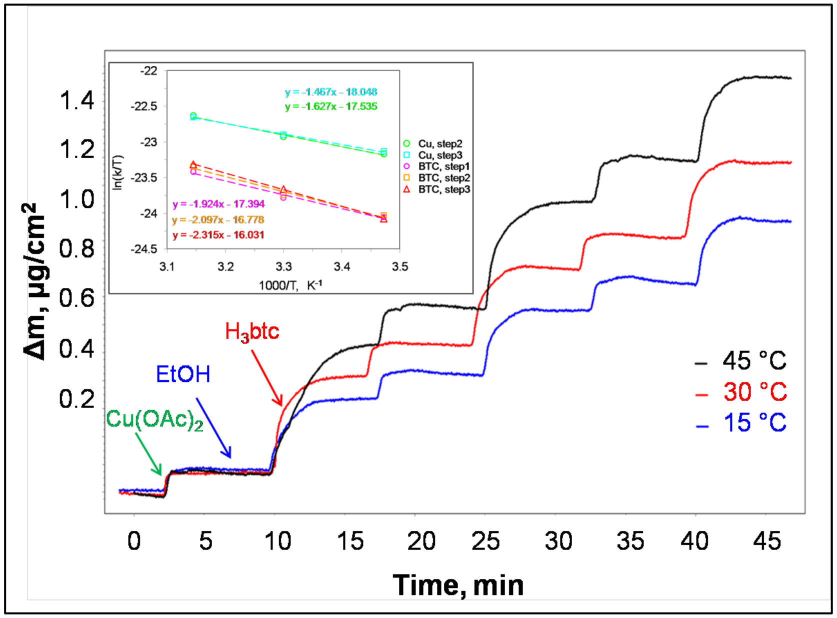
QCM crystal

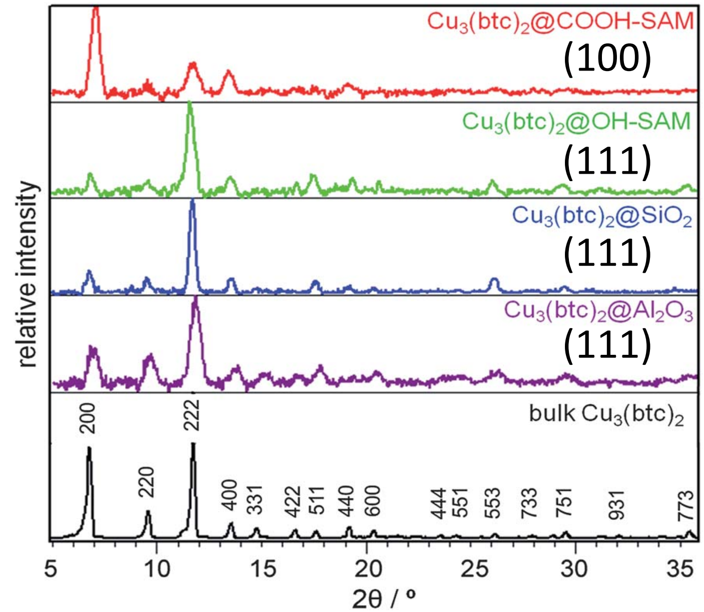


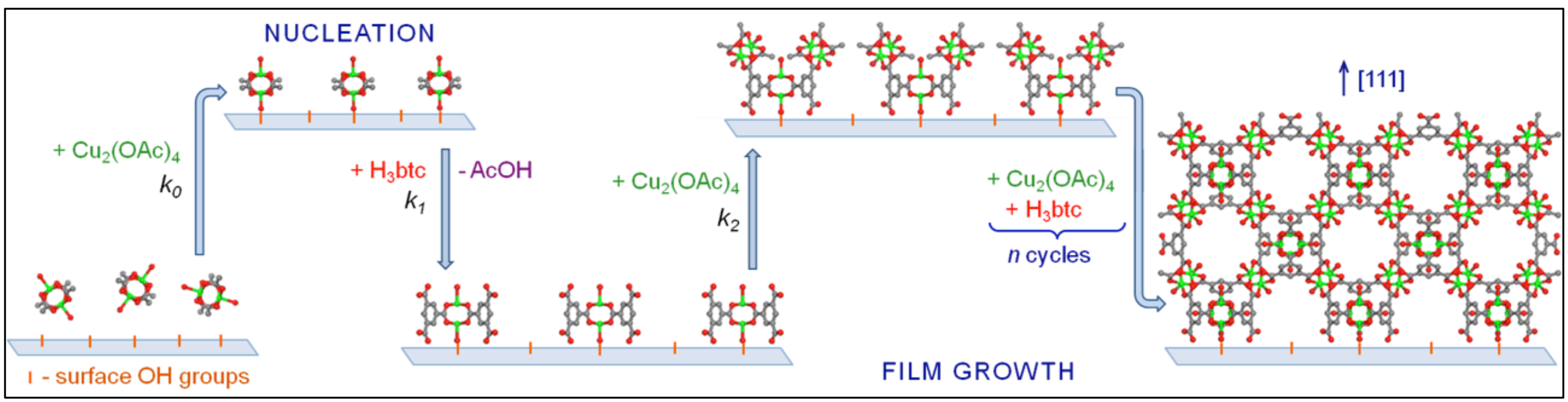


Automated MOF film growth with QCM capability

Layer-by-layer deposition: self-limiting growth with controllable orientation



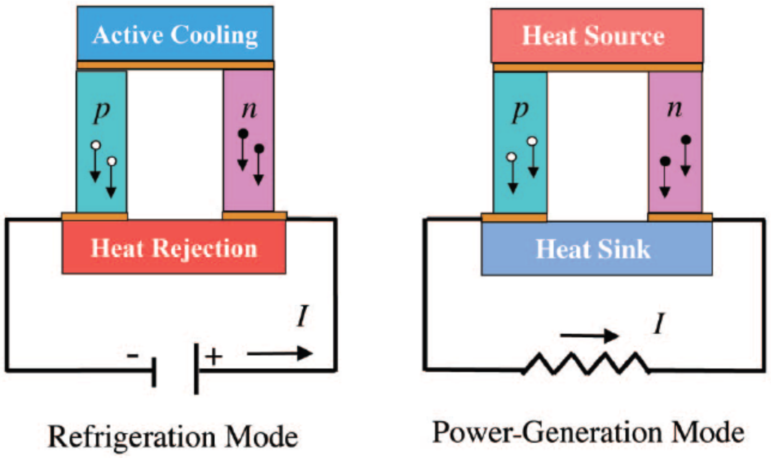


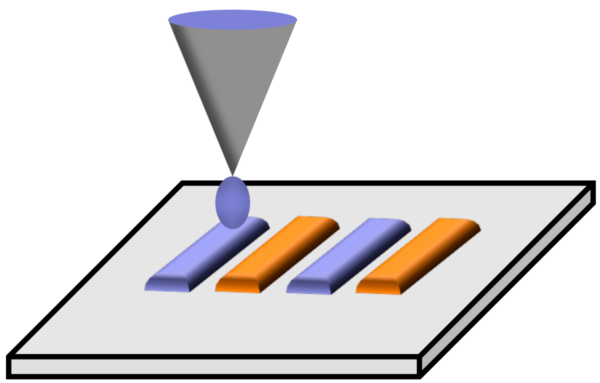


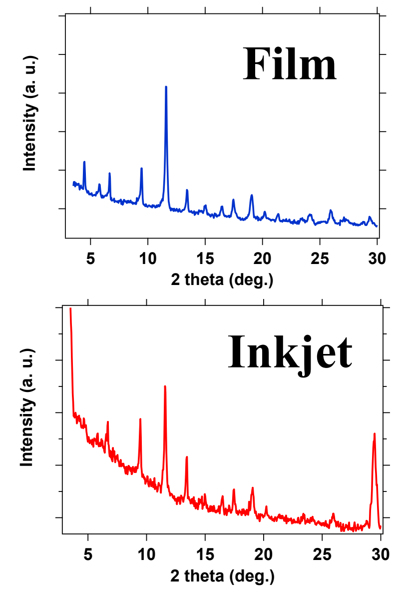
V. Stavlia et al. *Chem. Sci.* **3** (2012), 1531–1540

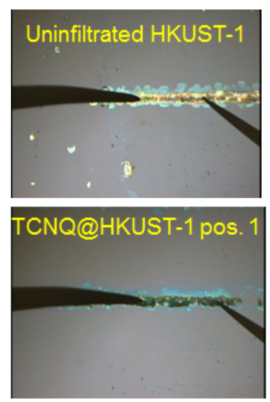
Inkjet deposition of conducing MOF

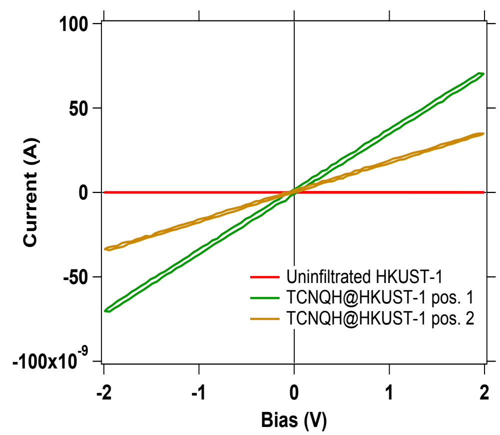
Practical TEs require thick, n- and p-elements



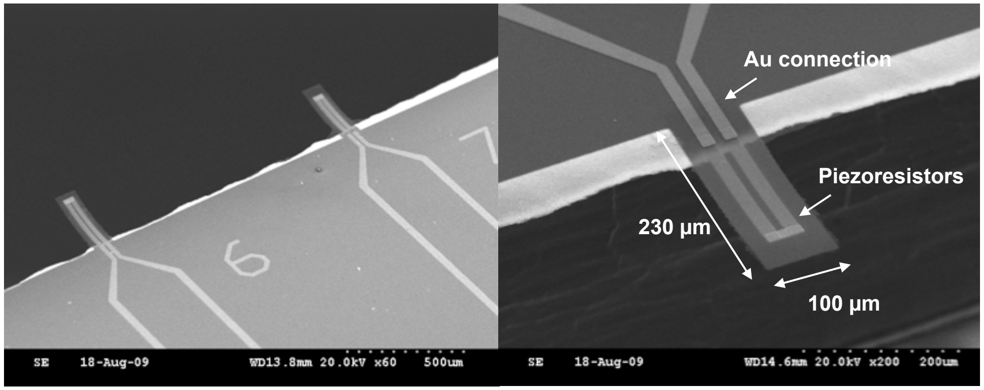




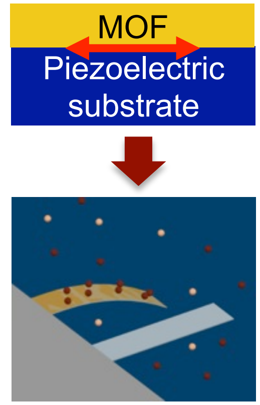




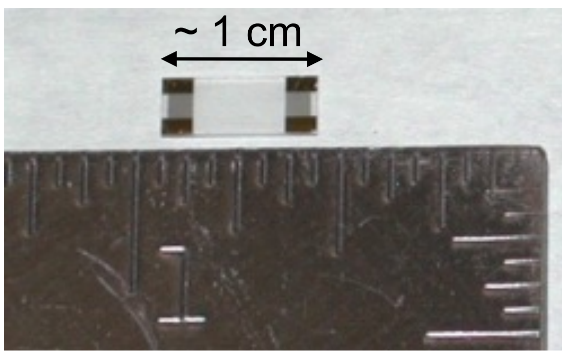
Sensing platforms for detection by mass uptake

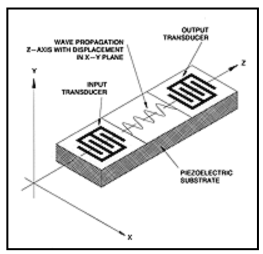


Microcantilevers (fg sensitivity)



Quartz crystal microbalance (QCM) (~1 ng/cm^2 sensitivity)

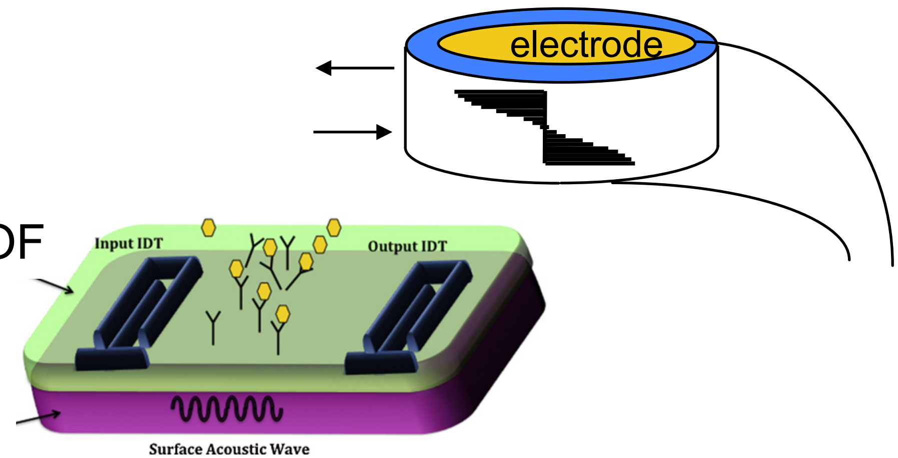




Surface accoustic wave (SAW) sensors (~ 0.1 ng/cm^2 sensitivity)

MOF

Piezoelectric substrate

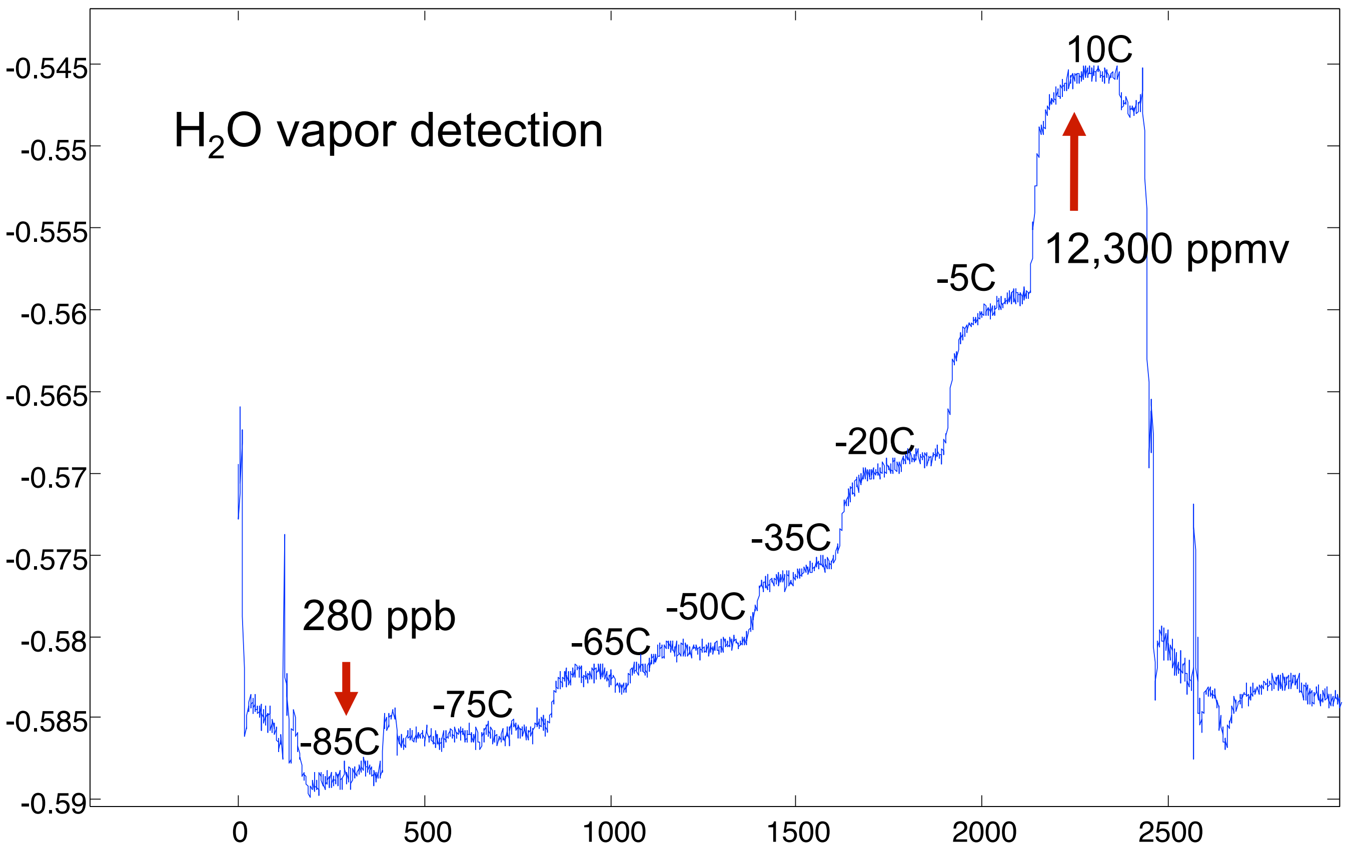


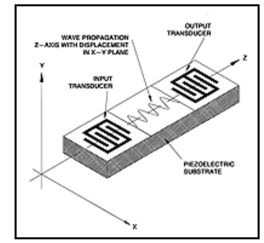
Recognition chemistries are required to enhance sensitivity and impart selectivity to the device

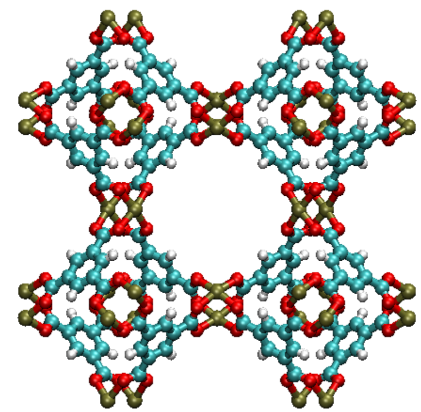
MOF-coated MEMS devices can compete with state-of-the-art sensors

SAW sensor coated with HKUST-1 ($Cu_3(BTC)_2$)

Sensor response > 4 orders of magnitude in H_2O concentration





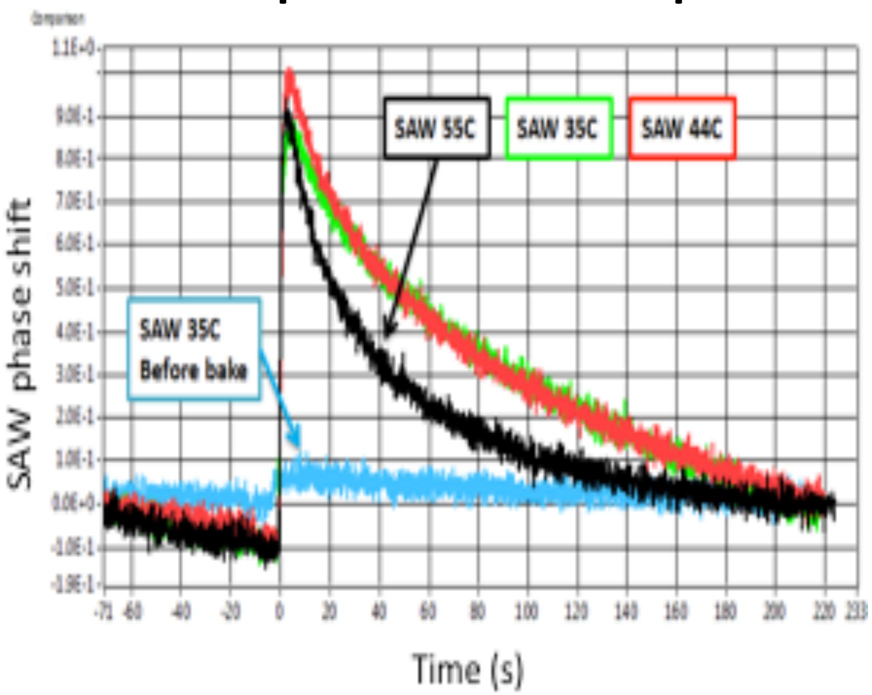


Cu_3BTC_2 (HKUST-1)

Robinson et al. *Analytical Chem.* **84** (2012), 7043

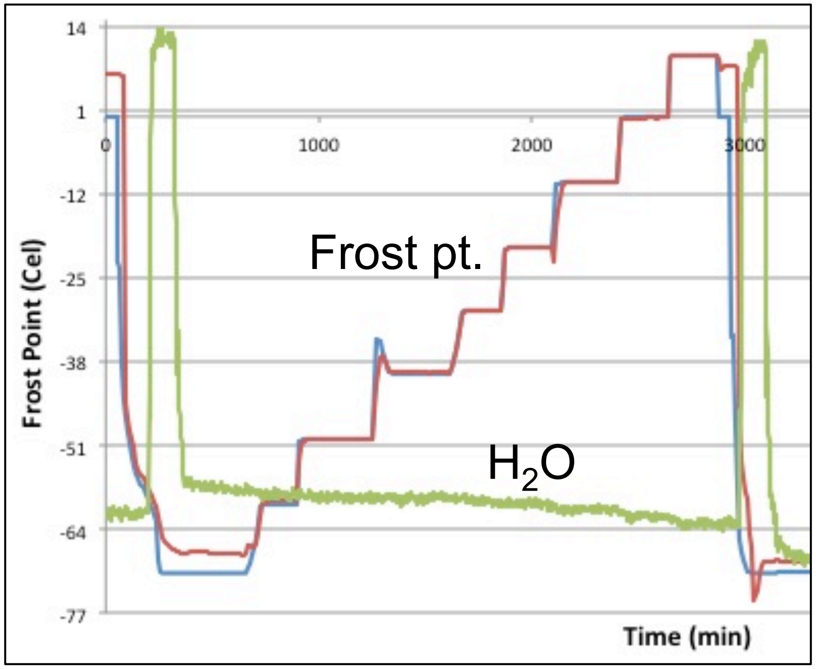
Response to acetone: ZIF-8 vs. HKUST-1

HKUST-1 (~100 nm film on SiO_2)
Response to acetone pulse



- **Fast response to H_2O**
- **H_2O LOD: < 1 ppm**
- **No response to N_2, CH_4, CO_2**

ZIF-8 (450 nm film on SiO_2)
Response to humidity



- **Acetone LOD: ~ 30 ppm**
- **No response to water vapor (above)**
- **No response to N_2, CH_4, CO_2**

MOFs as electronic materials combine features of inorganic and organic conductors

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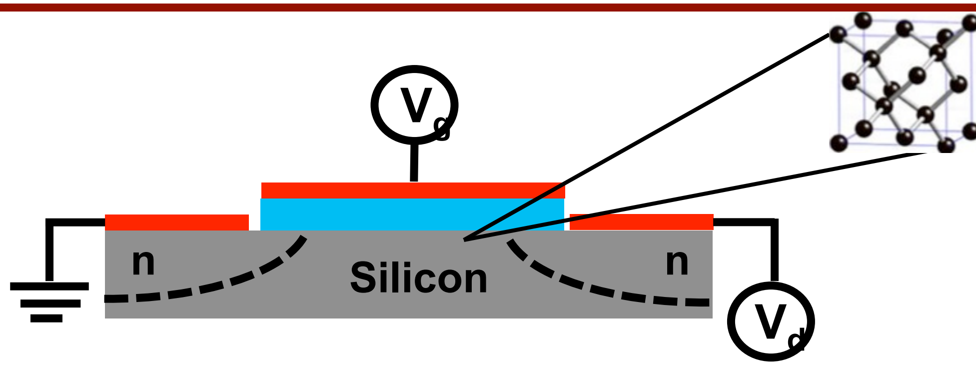
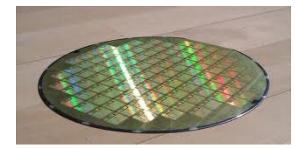
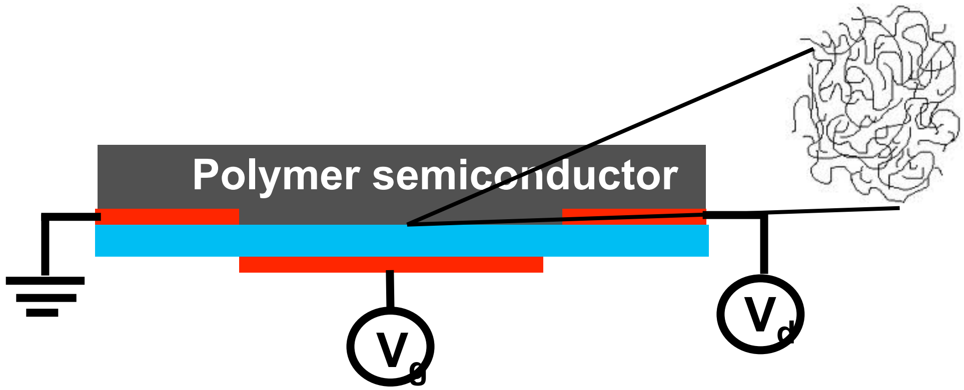


Crystalline inorganic semiconductor

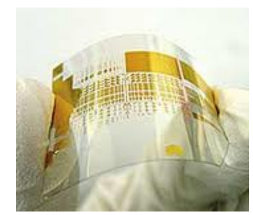
- High mobility
- Stability
- High cost
- Non-flexible
- Radiation damage

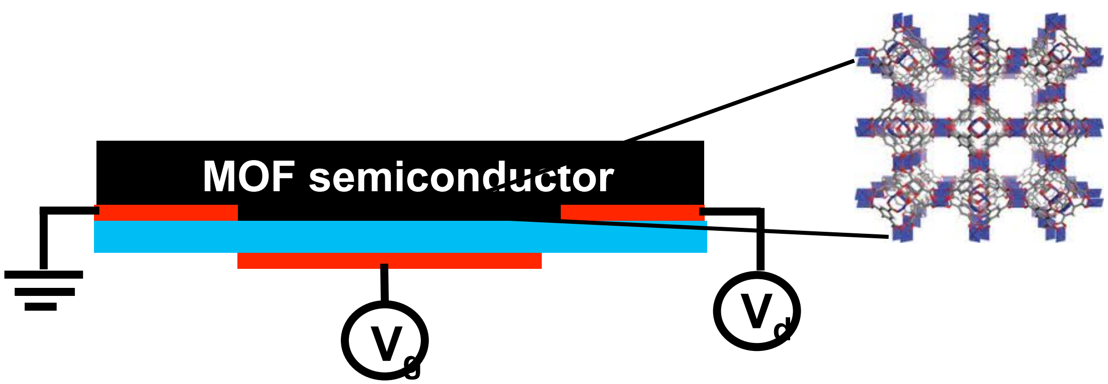




Disordered organic semiconductor

- Flexible
- Tunable w/ chemistry
- Low cost fabrication
- Poor mobility
- Instability
- Low free carrier densities



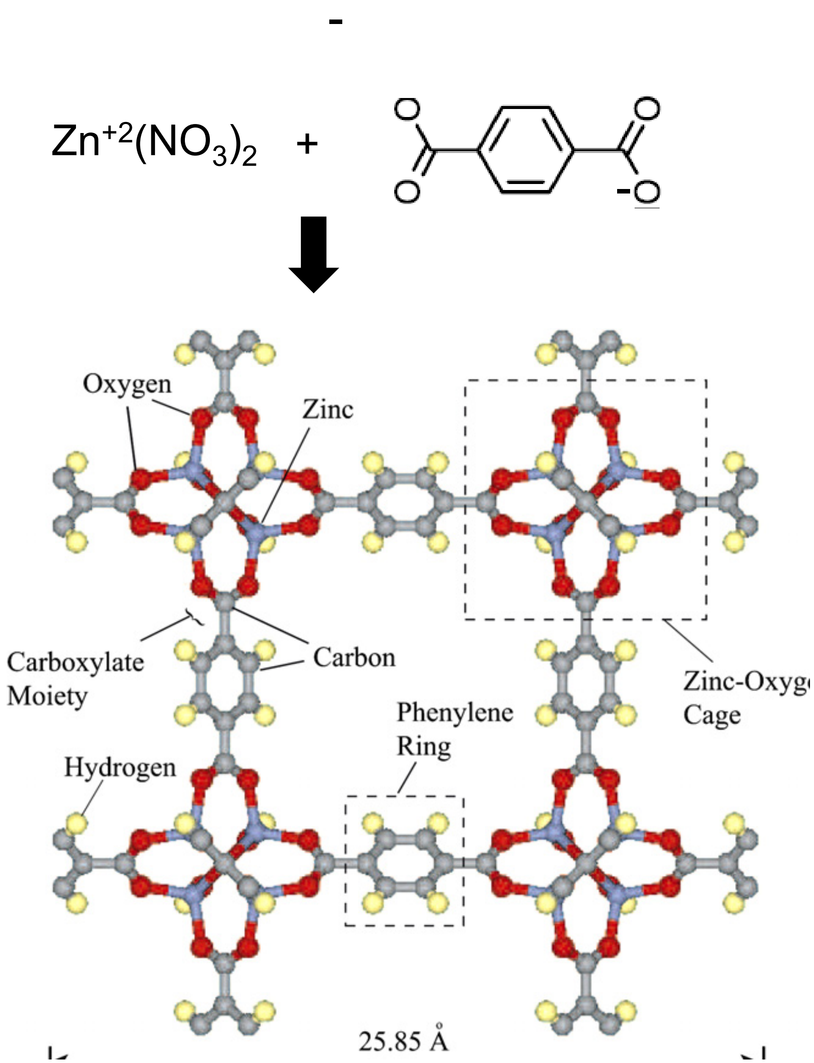


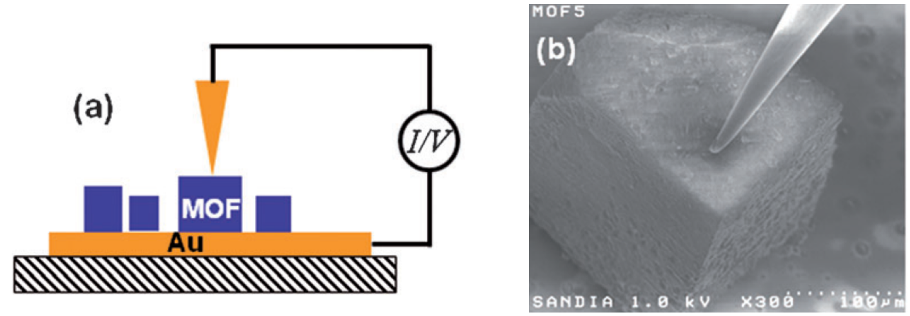
Crystalline MOF semiconductor

- Structurally flexible
- Tunable w/ chemistry
- Scalable to nanometers
- Low cost fabrication
- Reconfigurable electronics
- Rad-hard
- Novel electronic material

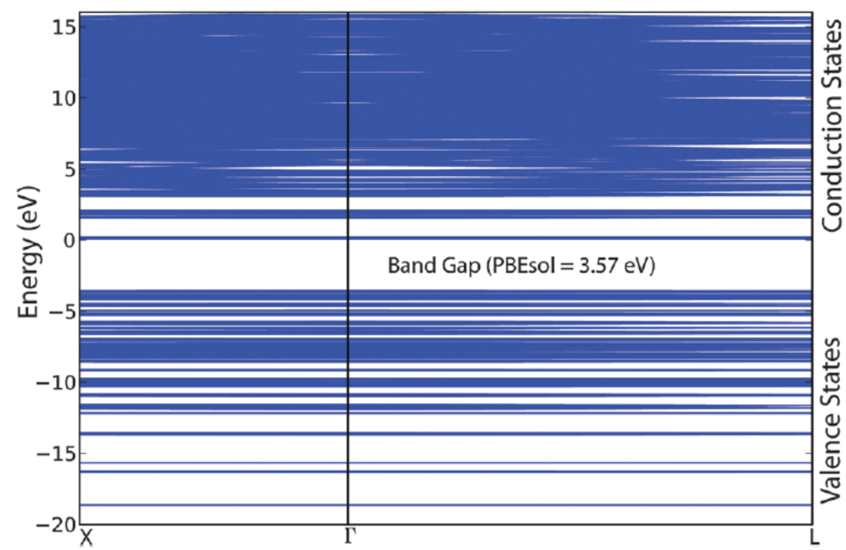
MOFs combine features of inorganic and organic materials

Most MOFs are Insulators, Lack Delocalized p-Network



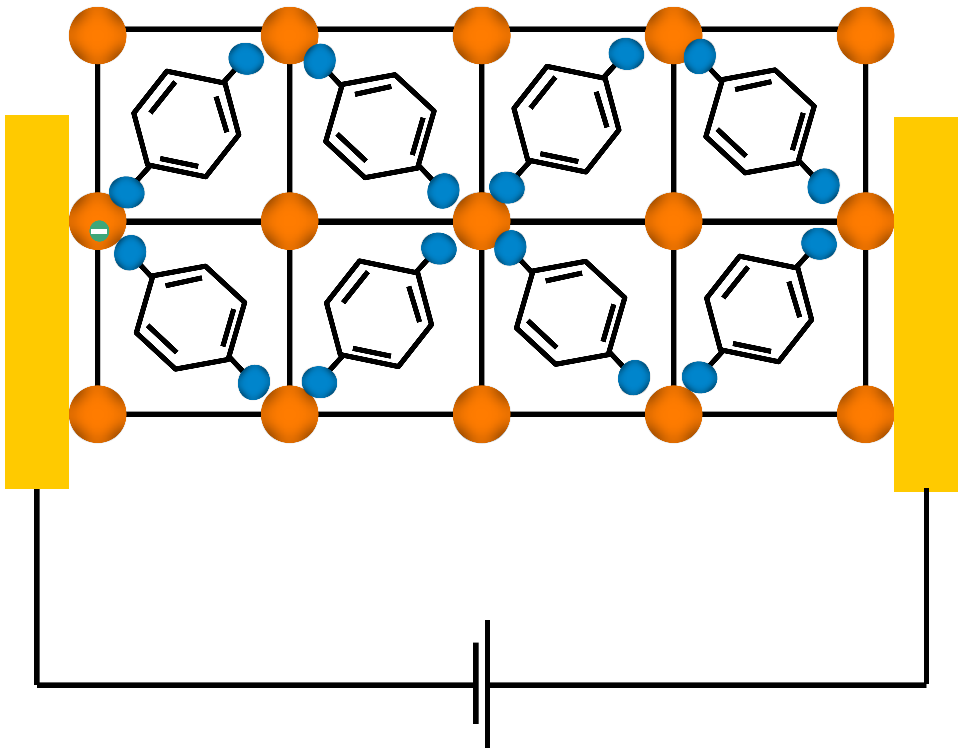


M. D. Allendorf, A. Schwartzberg, V. Stavila, A. A. Talin, *Chemistry – A European Journal* 17, 11372 (2011).



C. H. Hendon, D. Tiana, A. Walsh, Phys. Chem. Chem. Phys., 2012, **14**, 13120

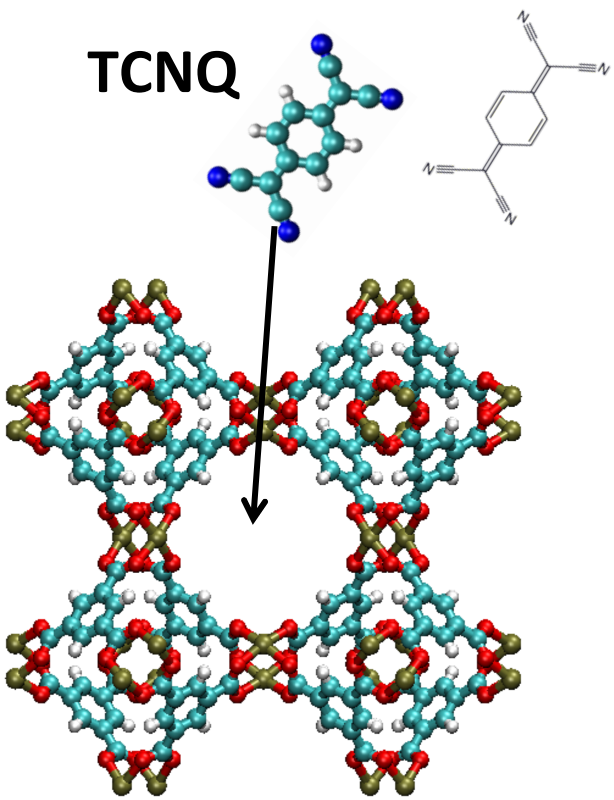
Can a 'guest' provide coupling between SBUs to create a conduction path?



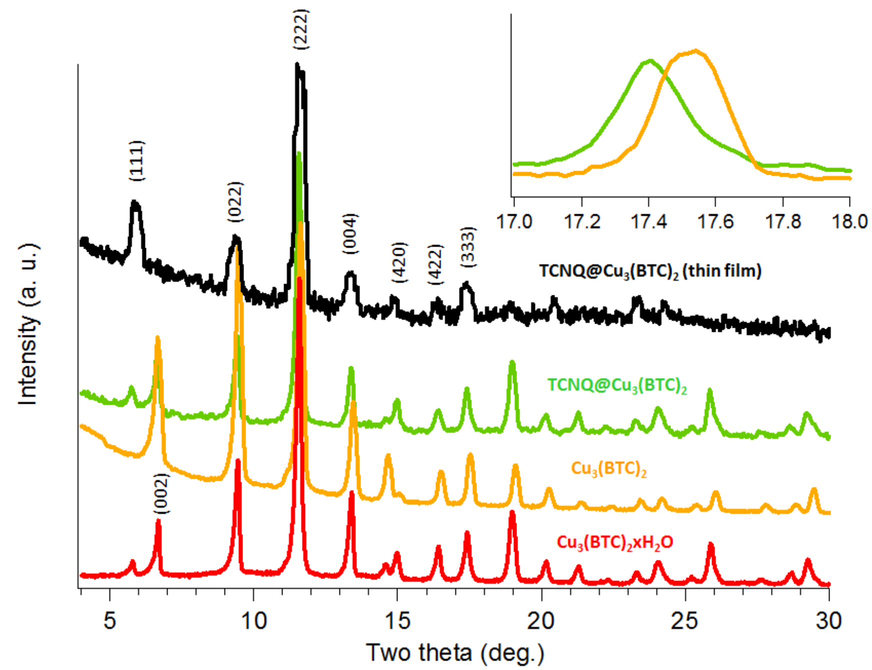
Requirements:

- Open metal sites
- Delocalized π-electrons
- Strong ligand-metal coupling

Guest@MOF: Emergent properties by infiltrating with guest molecules?

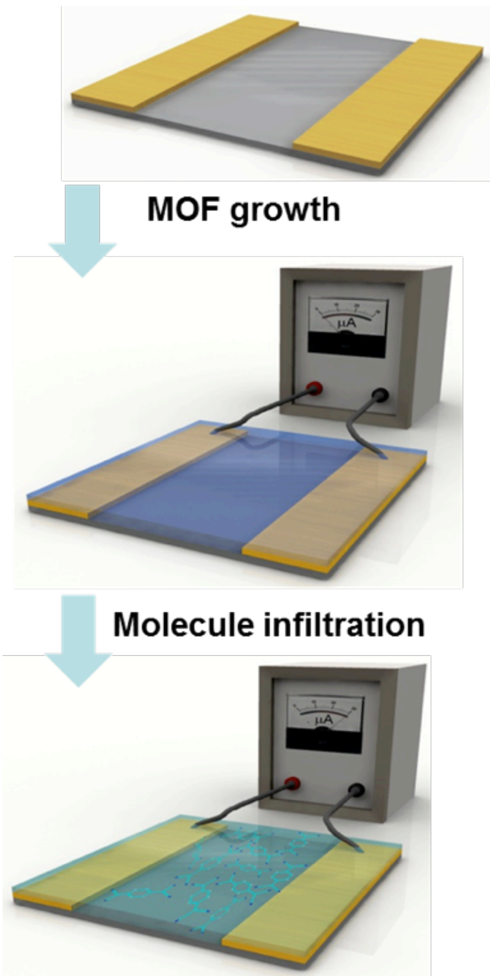


$Cu_2(BTC)_3$
(HKUST-1)

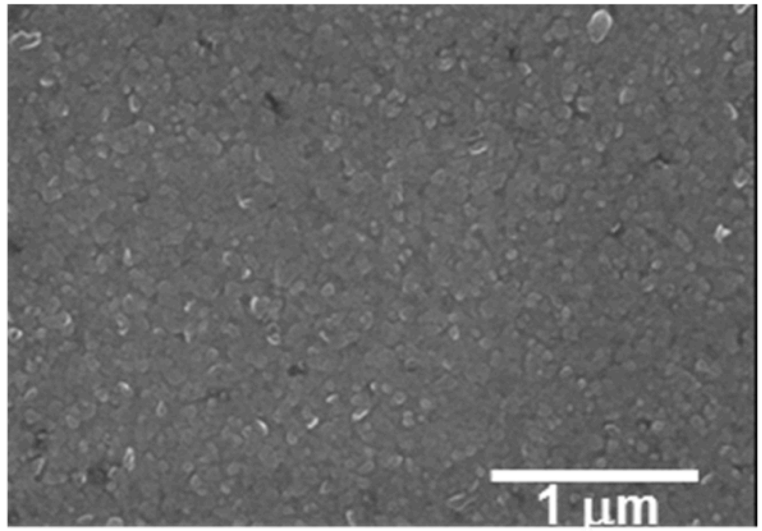


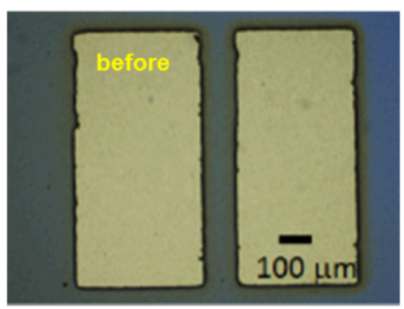
TCNQ loading: ~ 1 molecule/large pore

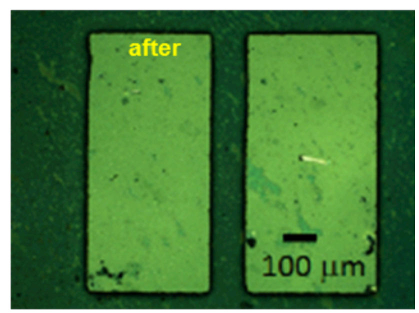
TCNQ→ $Cu_2(BTC)_3$ leads to color change…



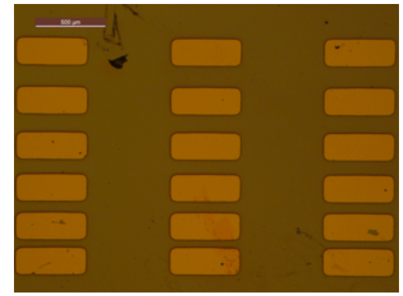
MOF film grown by layer-by-layer method



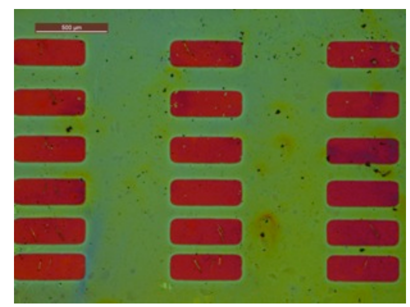




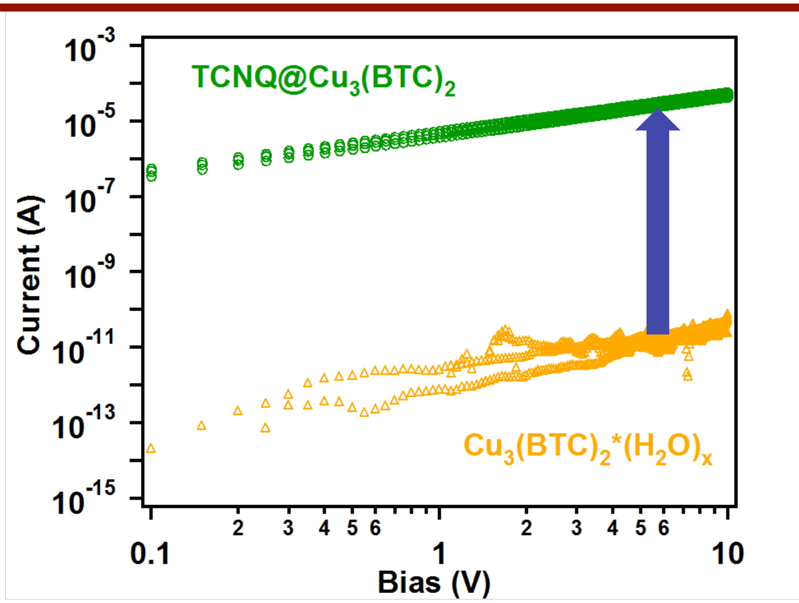
MOF film on SiO_x with Pt electrodes

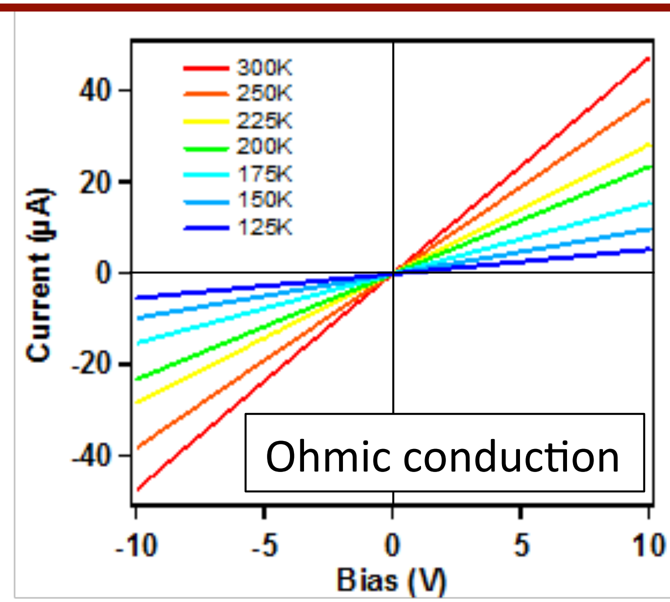


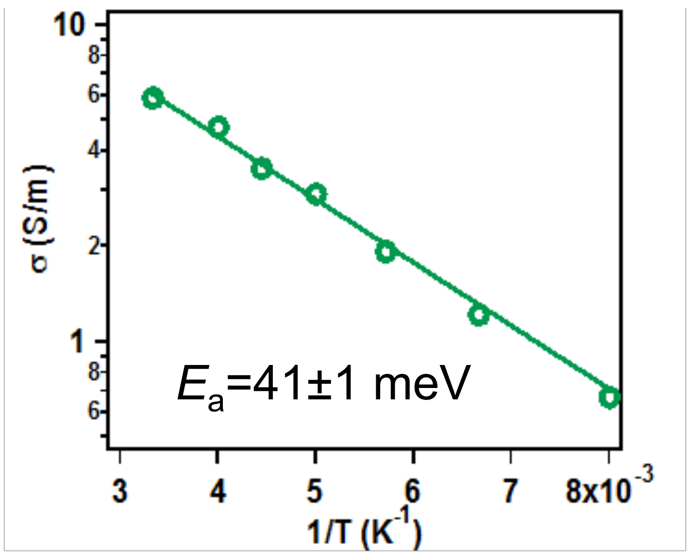
MOF film + TCNQ

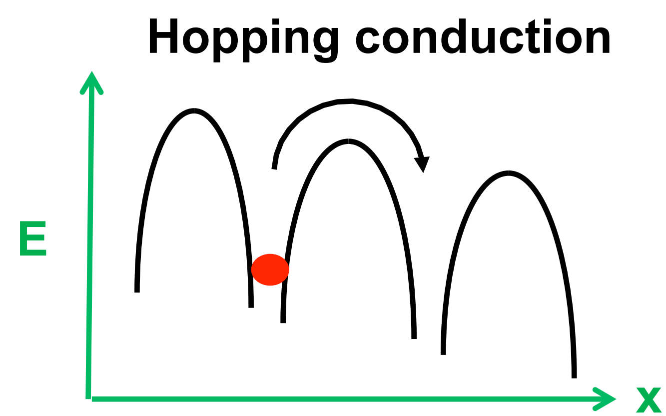


… and >10^7 increase in conductivity, air stable > 1 year



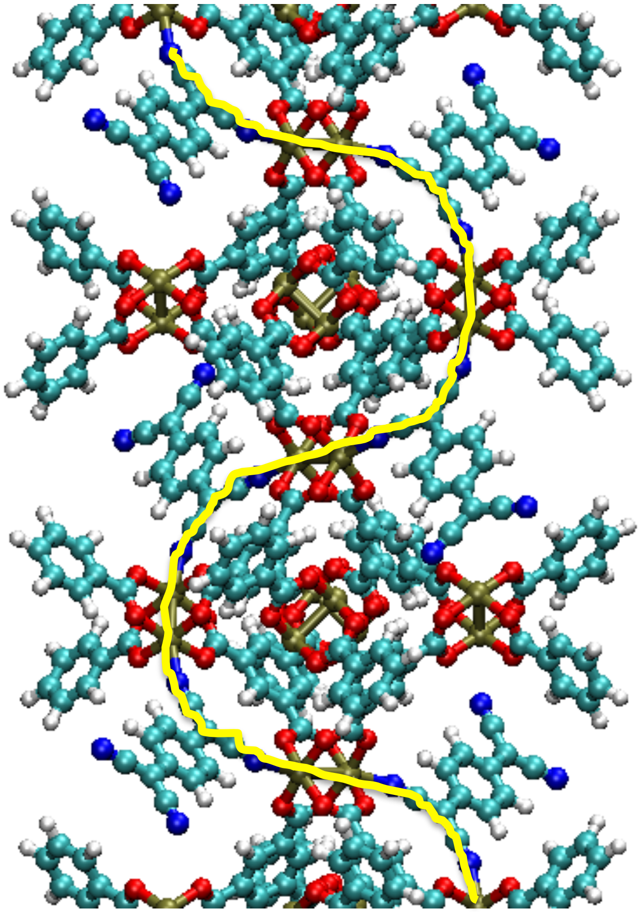


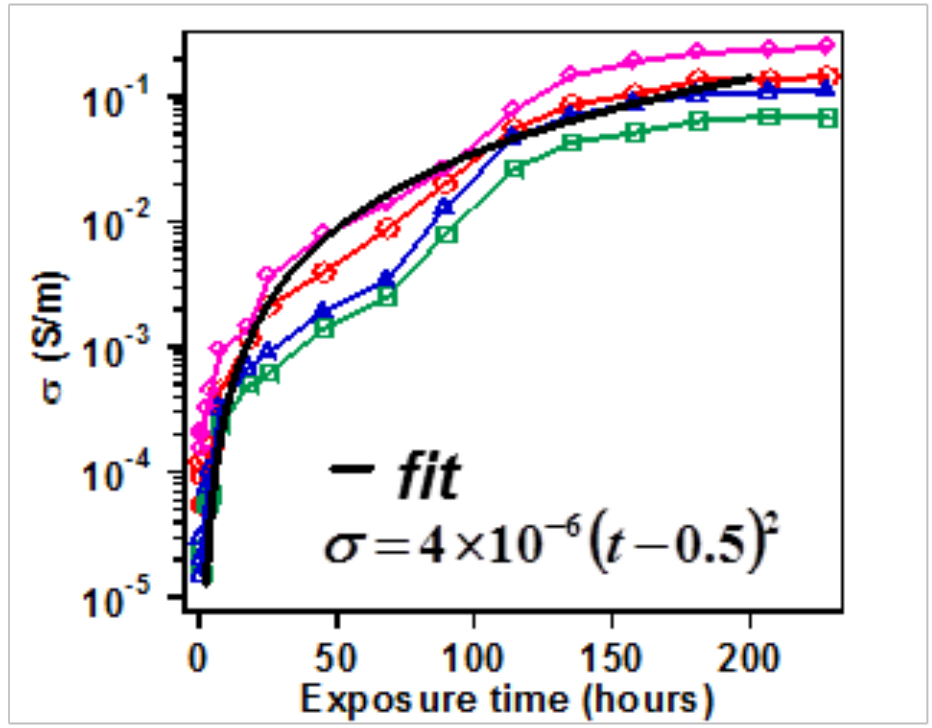




What is the mechanism?

Proposed conductivity mechanism: $Cu_2(btc)_4$ paddlewheels bridged by TCNQ



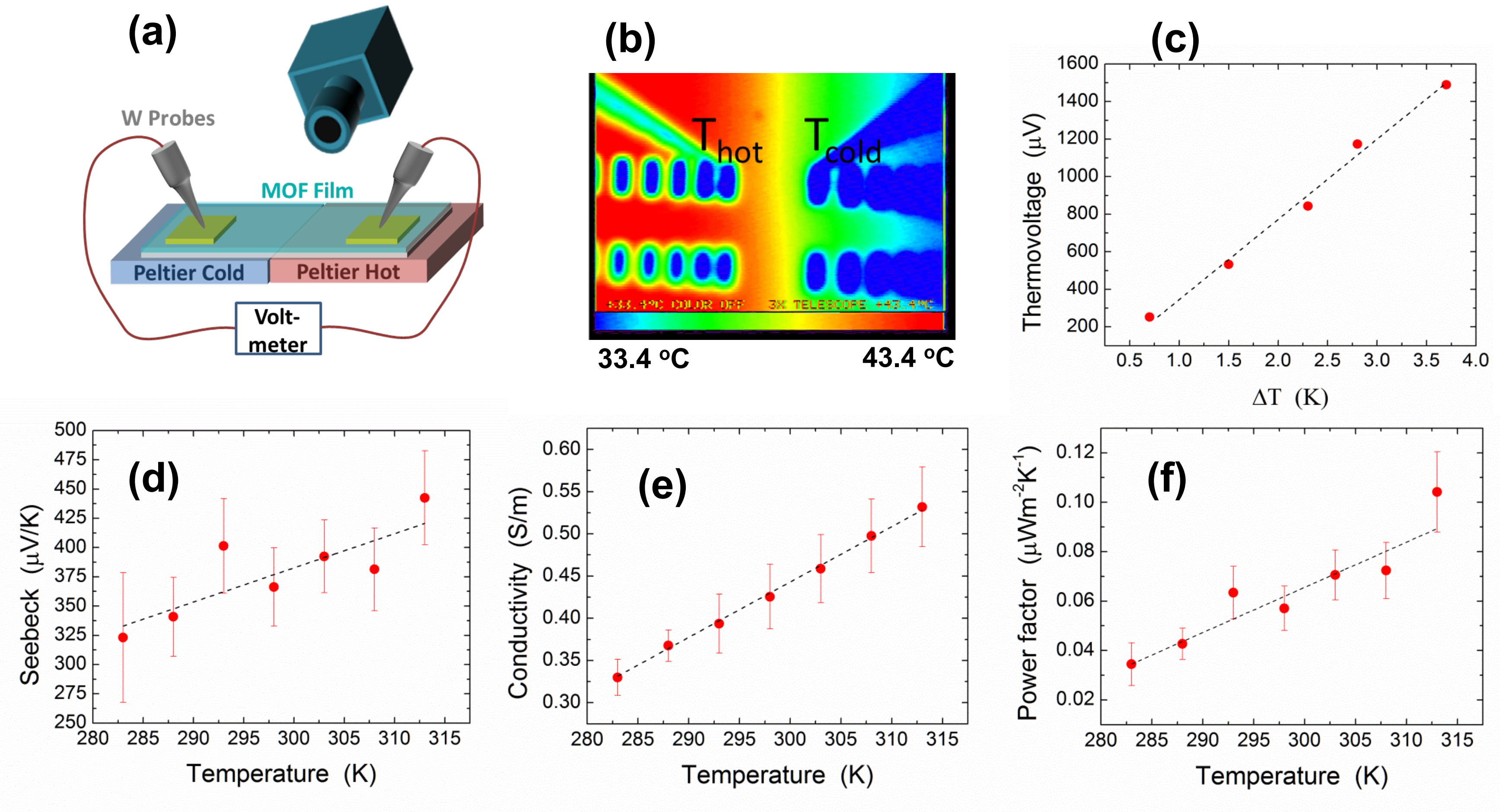


Percolation model

Continuous TCNQ@CuBTC pathway is achievable with 4 TCNQs

Experimental loading = 8 TCNQs/unit cell → two continuous pathways are possible

S, σ increase with temperature

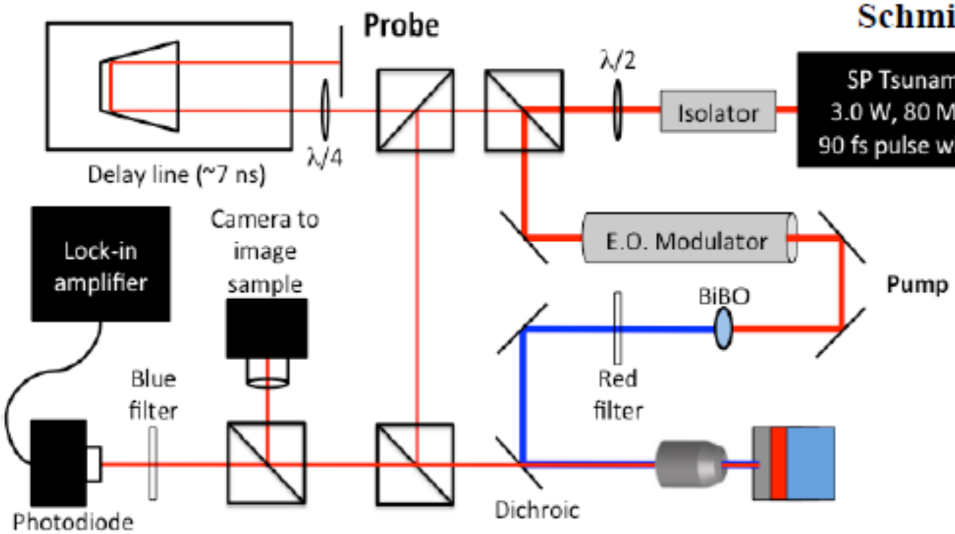


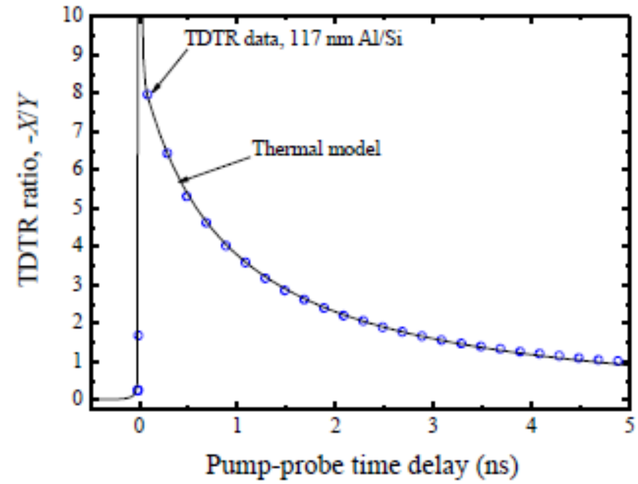
K. J. Erickson, F. Léonard, V. Stavila, M. E. Foster, C. D. Spataru, R. E. Jones, B. M. Foley, P. E. Hopkins, M. D. Allendorf, and A. A. Talin, *Advanced Materials, accepted*

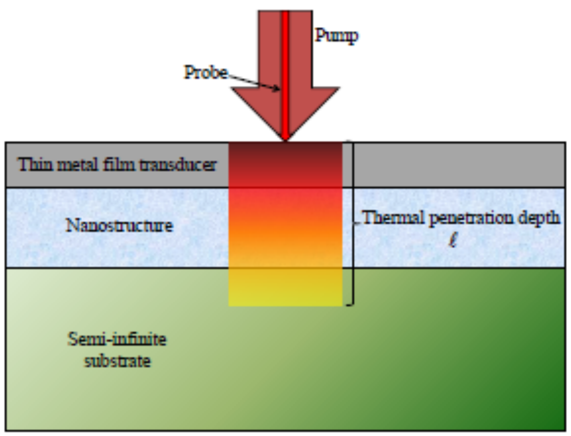
Thermal conductivity measured by Time Domain ThermoReflectance (TDTR) (P. Hopkins group)

Sandia National Laboratories

Hopkins *et al.*, *J. Heat Trans*. 132, 081302 (2010)
Cahill, *Rev. Sci. Instr.* 75, 5119 (2004)
Schmidt *et al.*, *Rev. Sci. Instr.* 74, 114902 (2008)







- Can measure thermal conductivity of thin films and substrates (κ) separately from thermal boundary conductance (h_K)
- Nanometer spatial resolution (~10's of nm)
- Femtosecond to nanosecond temporal resolution
- Noncontact

Large Seebeck, low κ, but σ still too low…

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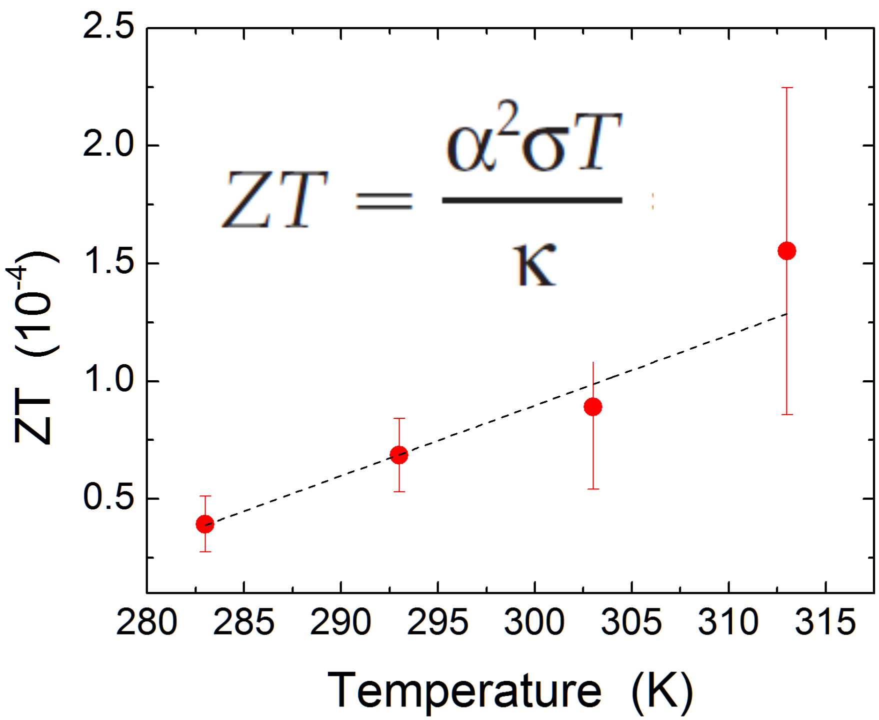

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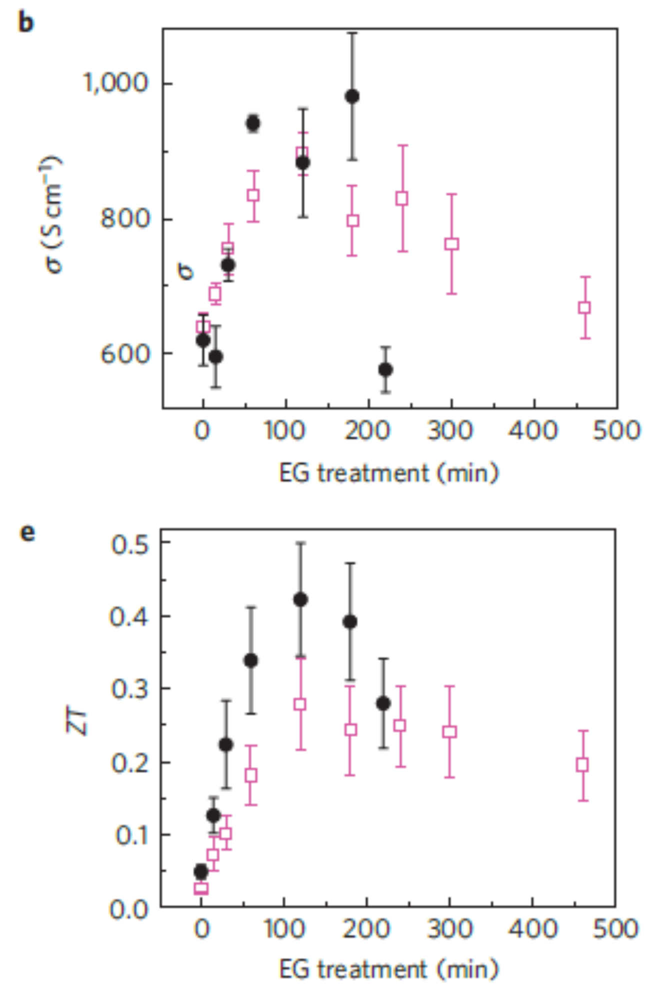

G. H. Kim, L. Shao, K. Zhang, K. P. Pipe. *Nat. Mater.* **2013,** *12*, 719

Four basic roles for MOFs in devices

- Adsorbant: provide sensitivity and selectivity (sensing)
- Electronic: passive (low-k dielectric)
- Electronic: active (sensing; thermoelectrics; logic)
- Light absorbing/emitting: energy harvesting, radiation detection
- Template or scaffold: ordered structures for improving exciton harvesting

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- Catalin Spataru
- Erik Spoerke
- Vitalie Stavila
- Alec Talin
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- Georgia Tech: Prof. Peter Hesketh

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- **U.S. DOE Sunshot Program**

SunShot U.S. Department of Energy

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NEES NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

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